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AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. XXIX.—*An Experimental Investigation into the Existence of Free Ions in Aqueous Solutions of Electrolytes;* by JULIUS OLSEN.*

VAN'T HOFF in 1887† showed that the gas laws of Boyle, Gay-Lussac, and Avogadro, hold also for dilute solutions. From considerations of osmotic pressure, theoretically and experimentally, he was able to apply Avogadro's law to solutions, and gave it as follows:

"The pressure which a gas exerts at a given temperature, if a definite number of molecules is contained in a definite volume, is equal to the osmotic pressure produced by most substances under the same conditions, if they are dissolved in any given liquid."

These laws may be combined in the well known expression

$$PV = RT$$

which holds for most substances, where P is the osmotic pressure and V, T, and R, as in the gas law, are volume, absolute temperature, and $= \frac{PV}{T}$ for a perfect gas, respectively, and includes Avogadro's law if we consider kilogram-molecules of the substances, as Horstmann has shown.

Van't Hoff found that the above expression held for most substances, but there were many important exceptions. These exceptions were the acids, bases, and salts; in these the osmotic pressures were greater than the law required. In other words, he found that the solutions with abnormal osmotic pressures were the electrolytes. He accordingly introduced into the expression the coefficient i and wrote it

$$PV = iRT$$

* An abstract of a thesis presented to the Graduate Faculty of Yale University for the degree of Doctor of Philosophy.

† Zeitschr. Phys. Chem., i, 481, 1887.

This coefficient would be *one* for "ideal" solutions and greater than *one* for the acids, bases and salts.

Arrhenius* showed, also in 1887, how these exceptions might be explained; and thus the law hold for *all* substances. The osmotic pressure, other things being equal, depends upon the number of particles present in a given volume of the solution, in the same way as the pressure of a gas depends upon the number of its particles. If then the osmotic pressure is too great, there must be more particles present than were put in. These substances must therefore be dissociated, i. e., the molecules split up into two or more parts. Arrhenius reasoned in this manner.

This same assumption had been made use of to explain the abnormal pressures of some gases; but on account of the chemical objections had not before been applied to solutions. Arrhenius accordingly brought forth again the electrolytic theory of Clausius, and established it, seemingly, by showing how to calculate the amount of dissociation.

Clausius had believed that "some of the molecules of an electrolyte are dissociated into their ions, which move about independent of each other." During electrolysis these momentarily free ions would be guided to their respective poles. According to this theory there is no direct decomposition of the electrolyte by the current, as was held by Grotthüss in his theory. It has been shown since the time of Grotthüss that electricity moves with the same ease in electrolytes as in metals, so there is no place for such work as decomposition.

From the activity coefficient (a), which he considers the ratio of the actual molecular conductivity to the maximum conductivity, i. e., the conductivity at infinite dilution, Arrhenius proceeds to show how to determine the coefficient i of the formula, and thus test the theory. By a comparison of the lowering of the freezing point of a liter of water, in which a gram molecule of the substance is dissolved, and i as calculated from the conductivity method, he found the agreement to within the limits of experimental error.

The theory has since been tested by a great many men, by the method of the lowering of the freezing point, the rise of the boiling point, osmotic pressure, conductivity, etc. There are seemingly some exceptions as shown by Kahlenberg† and others, but the preponderance of evidence is certainly in its favor so far. Some of these exceptions may be due to the somewhat limited knowledge we have of the true composition of some substances. And the law has its limitations, in the same way as the gas laws, and holds only for dilute solutions. The theory, at least, explains a great many phenomena that cannot be explained, at present, by any other means.

* Ibid., i, 631, 1887. † Am. Jour. Phys. Chem., June, 1901.

No direct experimental proof was attempted until Ostwald and Nernst,* in 1889, performed the following experiment. It will be given substantially in their own language.

A glass tube about 30 or 40^{cm} in length, provided with a stopcock, was drawn out to a fine capillary at one end. The tube was then partly filled with mercury and hung upright, with the capillary in a solution of dilute sulphuric acid. By suction at the upper end the mercury was drawn up and the sulphuric acid after it. When at a convenient height, about the middle of the capillary, the stopcock was closed and the liquid thus held in place. A platinum wire fused into the tube connected with the mercury.

A large glass flask was now filled with dilute sulphuric acid and insulated by placing it on a disk of hard rubber. The outer surface of the flask was coated with tinfoil and its neck varnished with shellac. The contents of the flask were connected with the sulphuric acid into which the capillary tube dipped, by means of a wet string. The positive pole of a small electric machine was brought in contact with the tinfoil, and the mercury of the capillary electrometer connected with the earth.

As soon as the electric machine was set in motion the mercury of the electrometer rushed up and at the same time bubbles of gas separated, which broke the thread of mercury in a number of places.

This is the explanation given.—By charging the outer covering of the flask with positive electricity, the negative electricity on the inner side would be attracted and held, while the positive would be repelled. The latter would go by the wet string to the capillary electrometer and then by the platinum wire to the earth. There is no closed current; the entire movement of electricity is produced by induction. This proves, they say, that free ions were present and that they moved.

They performed several other experiments, but all are on the same principle, and the same conclusions are drawn.

There seems to be good reason for the belief that the conclusion arrived at does not necessarily follow, but that we need further proof.

The potential of an electric machine is very high and the flask they used in connection with the capillary electrometer is really a condenser. As no substance insulates absolutely there must be in such an arrangement some current, and in such a restricted path there is a possibility of a considerable difference of potential. They do not say that the potential difference, between the two ends of the capillary electrometer, was measured. If this exceeded about 1·22 volts there was electrolysis and consequently a formation of gas bubbles.

* Zeitschr. Phys. Chem., iii, 271, 1889.

J. H. Pratt* shows that no current passes through a capillary electrometer below 1·22 volts. If no current can pass through a Lippmann electrometer before about the electrolytic limit of decomposition is reached, then this instrument is not a good one for this experiment.

In order further to test the capillary electrometer when connected for some time to voltages below 1·22, I made an instrument as follows:

A glass tube about 15^{cm} in length was drawn to a capillary at about 5^{cm} from one end. Into this shorter portion a platinum wire was fused. The tube was then filled with mercury and dilute sulphuric acid and inverted into a beaker containing dilute sulphuric acid and mercury. A cork was put on the upper end, and by releasing this a little the boundary between the mercury and sulphuric acid could be brought into the capillary. A space was left above the mercury so that it could recede when connected up to a Daniell. A platinum wire connected with the mercury in the beaker.

In this form the instrument, so far as its effective action is concerned, is exactly the same as that used by Ostwald and Nernst.

It was connected up to a Daniell of about 1·05 volts for hydrogen polarization and watched every few minutes for five hours, but no bubbles of gas were observed. It was afterwards connected up at the same voltage for eight hours with the same result.

Incidentally it may be stated that it was found that, if the tube was sealed at the upper end and entirely filled with mercury so there was no chance for it to recede, bubbles were formed in a few minutes, first at 1·05 and later with a new tube and new mercury at about ·88 volts.

In 1888 Ostwald† cites the following as a proof of the existence of free ions in solutions, but does not perform the experiment.

Let two vessels, A and B, be filled, for example, with a solution of potassium chloride, insulated and connected by a siphon filled with the same liquid. Now let a negatively charged body, K, be brought near to A; it will act inductively upon the system. A will become positive and B negative. If now the siphon be removed and then the body K, A will remain positive and B negative. To discharge A we can connect it with the earth, and the potassium ions, which are positive, will give up their charge and become atoms. These would act upon the water, forming potassium hydroxide, and hydrogen, which would escape from the solution as a gas.

* This Journal, 1888 † Zeitschr. Phys. Chem., ii, 1888.

Ostwald says that the amount of gas liberated would be too small to be seen, and so, as before stated, he does not attempt the experiment, but a year later, together with Nernst, gives the experiment previously mentioned.

It was believed that an electrostatic charge would attract and repel the unlike and like charged ions respectively. And as it is the ions which in giving up their charge produce a current, then if these ions could be guided by an electrostatic charge we should get a current with electrodes indifferent to the solution, and be able to detect it with a sufficiently delicate galvanometer.

These were the beliefs upon which the following investigation was founded.

The experiments were performed on a brick pier capped with a granite slab and entirely independent of any vibration of the building. A delicate Rowland galvanometer together with a telescope and scale was used. The scale was about $156{\cdot}0^{cm}$ from the mirror of the galvanometer. The deflections were read to $0{\cdot}1^{mm}$.

A U-tube was first used, into which were placed platinum wire electrodes. The wires were wound into a spiral in order to increase the surface exposed. Before putting them in, the electrodes were heated to a white heat in a blowpipe flame. Distilled water and a trace of sulphuric acid was used. It was found that the cell always gave a deflection; however, it was intended to take the deflection first, before an electrostatic charge had acted upon the solution, and then taking out the electrodes, let a charge from an electrophorus act upon the solution for some time and then put in the electrodes and take the deflections again.

It was found that an electrode taken out of dilute sulphuric acid and exposed to the air while the other remained in the solution was, when replaced, strongly negative. As this effect was so decided, and the exposure of the two electrodes could not be made of exactly the same duration, nothing could be gained from this method.

A cell was now made from a low round beaker about $53{\cdot}0^{cm}$ in diameter. Platinum foils $2\times2{\cdot}5^{cm}$ were welded to platinum wires which were run up through corks in a piece of wood that served as a cover for the cell. The foils were bent so as to fit around the curvature of the beaker and be about $2{\cdot}0^{mm}$ distant from its edge. The cover of the cell was held in place by small nails driven into it from the under side, and it could be turned around so as to bring the electrodes into any desired position around the edge of the cell.

The cell was placed on a wooden stand in such a way that the

disk of an electrophorus could be brought as close as I pleased to either electrode. 10, 5, 1 and $\frac{1}{2}$ per cent solutions of sulphuric acid were tested in this cell. The deflections just after the electrodes were put in the solution were very large and the cell could not be worked to any advantage until after a couple of days. The deflections with the more dilute solutions were not so large, and thus it did not take so long for them to get into working condition.

The electrophorus disk did not hold the charge over 8 or 10 minutes and had to be recharged. Every time a charged body was brought near to the cell, although the galvanometer circuit was open there was a considerable deflection due to ordinary electrostatic induction, and this would show itself also on closing the circuit to take a deflection. It was necessary then to avoid this as much as possible, and this could be done if the charge could be retained for a considerable time. The knobs of two Leyden jars were then placed close to the opposite electrodes and charged, the one positive and the other negative, by a friction machine. The jars of course hold the charge much better, but the effect did not seem to be very decided, which is perhaps due to the small surface exposed by the knobs.

In order to have a charge that would waste but slowly and at the same time have a considerable surface exposed, I connected the knobs of two Leyden jars to the disk of an electrophorus. The disk was about 21·0^{cm} in diameter and was generally brought to within about 2·0 or 3·0^{cm} of the cell and the knobs of the jars charged with the friction machine. The intensity of the electrostatic charge was judged, partly, by the induction produced while charging, and as this arrangement gave by far the greatest induction, it was believed to have the greatest effect on directing the ions, as was found later to be true. The friction machine gave a spark of from $\frac{3}{4}$ to 1 inch in length. The induction while charging is considerable, and although it seems to be about the same in whatever position the electrodes or disk are placed, so long as the charge is of the same sign, and although the recharging, with the jars, need be done only every 20 or 30 minutes, yet it was thought best to charge the jars only when the electrodes and jars are always in the same relative position.

The following positions were used and will be designated as follows:—Positions (1), (2), (3) and (4), figure 1.

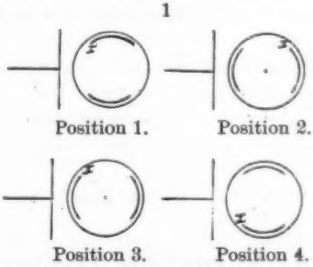
The T-shaped figure represents the disk,which can be charged by the jars and the electric machine. The cell is represented as seen from above. The arcs of circles represent the platinum electrodes.

The jars in connection with the disk were charged only when in positions (1) or (4), and discharged before the electrodes were turned into positions (2) or (3).

The galvanometer circuit is kept open except at the moment of taking a deflection. The direction of the galvanometer needle was determined beforehand.

The time between each deflection in the different series was generally 2 or 5 minutes. I will describe a 20-minute series, deflections being taken every 2 minutes, starting from position (1).

Before the jars were charged, the deflections were taken in position (1) every 2 minutes for 20 or 30 minutes or until the deflections became about uniform; then the cover of cell together with the electrodes were turned through 90° into



position (2), say. The turning was done very slowly and carefully so as not to disturb the liquid more than necessary, and care was also taken to avoid shaking or turning the cell. The deflections were then taken in position (2) every 2 minutes for 20 minutes, and then the electrodes were turned 180° through the first position into position (3), and the deflections taken in that position every 2 minutes for 20 minues. These readings would indicate the condition of the liquid at positions (2) and (3) before being acted upon by an electrostatic charge, and comparing these readings with the readings after the solutions has been acted upon by a charge would show the effect of the charge.

After the condition of the liquid was determined as above stated, the electrodes were turned into position (1) and the jars in connection with the disk charged positive or negative by the friction machine. The charge was allowed to act for the same interval of time as was used before, namely, 20 minutes, and the deflections taken in this position also, in order to keep the cell always in the same condition, that is, deflections were taken every two minutes throughout the entire experiment. If the cell is allowed to rest even a few seconds over the regular interval, a change in the amount of the deflection is noticed. The cell runs down quickly and recovers quickly.

If the deflections in any direction are large at the beginning of the observations, the direction cannot be reversed by this charge, and this method and the effect is only a differential one, but if the cell is in a more stable condition the directions can be reversed, and this was done scores of times.

The induction produced when the jars are discharged is of course in the opposite direction from what it is when charging, but it is not large and does not appear in the third reading of 2-minute intervals. Diffusion acts against the heaping up of positively or negatively charged ions in any part of the liquid, and this often appears in the last observations of a 20-minute series.

A solution of potassium hydroxide and a solution of potassium sulphate were also tested by this method, using platinum electrodes as before, with the same results as with dilute sulphuric acid.

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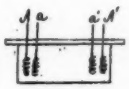
Top view



Side view

Incidentally it may be mentioned that the induction produced, in the galvanometer circuit, by bringing up a charged body to the cell was of about the same order of magnitude whether there was any liquid in the cell or not.

One acid, one salt, and one base were used in these experiments. The only reason for choosing these particular ones was, that it was necessary to employ some substance which on being decomposed and set free would not affect the platinum electrodes, and it was desirable also to have substances whose ions were known to have a considerable velocity.

Distilled water was always used.

It was now thought that it would be interesting to study the effect of an electromotive force, less than the decomposition value, upon an electrolyte. Accordingly the following experiments were performed:

No electrostatic charge was here employed.

A solution of different percentages of sulphuric acid was put into a cell having four platinum electrodes. The cover of the cell was so made that the inner or middle electrodes could be rotated independently of the outer.

The two inner electrodes a and a' were connected to the galvanometer circuit, and the two outer electrodes A and A′ were to be connected to a Daniell. a and A were about 8·0 mm apart, and a and a' about 50·0 mm apart. The circuit to the

galvanometer was closed only while taking a deflection, and this was never done while the circuit of the Daniell was closed.

The connections were generally made as follows (fig. 2):

If a of the galvanometer circuit was found to be negative and a' positive when beginning the observations, then A was connected to the positive pole and A′ to the negative pole of a Daniell. After the Daniell had been connected thus for a few minutes, it was disconnected and the sign of a and a' tested by closing the galvanometer circuit. a might still be negative and a' positive, but by connecting up the Daniell the same way and repeating this, a could always be made of the same sign as A. Then keeping the circuit of the Daniell open and leaving everything else as before except turning the electrodes a and a' through an arc of 180°, so that they exchanged places, and after a few minutes closing the galvanometer circuit, it was found that the direction of the deflection was reversed. Turning back to the first position would reverse it again. This could be repeated several times without connecting up the Daniell again.

This would show that the liquid in the neighborhood of a positive pole connected to a Daniell is charged with positive ions, or around the negative pole is charged with negative ions, or both.

The electrodes connected to the Daniell became polarized and remained so for some time. The same results were obtained, however, if after disconnecting the Daniell, the electrodes were discharged by short circuiting them. In this case the Daniell had to be connected for a longer period to obtain the same result, but this was all.

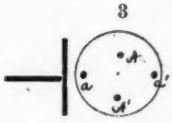
By connecting the Daniell to the *inner* electrodes and the galvanometer to the *outer* electrodes, the results were the same but it took a longer time.

This would show that the ions diffuse in all directions, but that they are more numerous between the electrodes.

Richarz and Lonnis* have shown, by means of the reaction with titanic acid, the presence of hydrogen peroxide at the cathode in dilute sulphuric acid at electromotive forces too small to produce an evolution of gas. But no hydrogen peroxide was discovered at voltages below one Daniell.

The same results as those above mentioned with one Daniell were obtained in my experiments by using $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$ the voltage of a Daniell, but it took a correspondingly longer time. When the electrolytic limit of decomposition was reached, the deflections became very large and the solution responded more quickly to the influence of an electrostatic charge, but the

*Zeitschr. Phys. Chem., xx, 1896.



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direction of the deflections were the same as before. In the experiments of the effect of an electrostatic charge on a solution which has been subjected, first, to an electromotive force less than the electrolytic limit of decomposition, and then on the solution after the decomposition limit has been exceeded, a cell of the form shown in fig. 3 was used.

a and *a'* are the electrodes connected to the galvanometer circuit; A and A' are the electrodes which may be connected to the Daniell, and T is the disk which may be charged electrostatically.

As has been stated, a larger and more prompt effect was noticed when an electromotive force, although below the decomposition value, was connected up to a cell and then an electrostatic charge brought up than when no current had previously been allowed to act upon it. Also that a pair of electrodes became of the same sign as the nearest electrode connected to a Daniell, this also although below the decomposition value of the solution.

This may be explained as follows:

Either the ions already free are heaped up around the electrodes as they become charged by the current, or the current, although below the decomposition value for the evolution of gases, yet decomposes the electrolyte. Accordingly the following experiment was performed.

According to H. C. Jones,* strong acids and bases are completely dissociated at dilutions of about one one-thousandth normal solutions. If there is complete dissociation, then there are of course no more molecules to be decomposed by the current unless the water decomposes. I took, in order to be sure of complete dissociation, a one-fourteen-hundredth normal solution of sulphuric acid, and using the cell shown in figure 2, subjected the outer electrodes A and A' to a potential difference of about 0·8 volt.

After taking several deflections by closing the *aa'* or galvanometer circuit, in order to get the cell into a somewhat steady condition, and noting the direction of the deflections, the AA' circuit was connected up to a potential difference of about 0·8 volt from a Daniell, in such a direction as to increase the deflections in the galvanometer circuit. It did increase the deflections and on reversing the direction of the current from the Daniell, the deflections in the galvanometer circuit decreased and finally reversed.

Here no decomposition of the sulphuric acid could take place as it was completely dissociated before, and the voltage

* Theory of Electrolytic Dissociation, p. 190.

was too low to decompose the water; hence it would seem that there are free ions present and that they are heaped up around the electrodes when they are charged by a Daniell.

Some time after the preceding experiments the following were performed.

It is known that when two metal electrodes, as for example copper, are placed in a solution of their salt and the circuit closed, that the smallest potential difference between them will give rise to a current and the metal will be dissolved from the anode and deposited on the cathode.

If then we take two copper electrodes, weigh them carefully and they on being placed in a solution of copper sulphate do not give too decided a deflection, we may be able to change the direction of the deflection by an electrostatic charge and then on short circuiting them and keeping up the charge we should get a diminution in weight of the anode and a gain in weight of the cathode.

Copper wires were bent into a flat zigzag form, in order to give a larger surface exposed and at the same time so that they might be placed near to the edge of the cell and consequently as near as possible to the electrostatic charge.

The electrodes were marked, cleaned in nitric acid, washed, dried and carefully weighed. The electrodes on being placed in the solution gave a decided deflection, but I was able to reverse this direction with two ordinary sized Leyden jars connected to a disk of an electrophorus and charged by a friction machine. The circuit was then closed through the galvanometer, and the electrostatic charge renewed occasionally by giving the electric machine a few turns. If the circuit was closed without any external resistance as by a short thick wire, the cell ran down quickly and sometimes gave a deflection in the opposite direction, so the circuit was made through the galvanometer. The circuit was kept closed for about three-quarters of an hour, breaking it only while recharging jars. The electrodes were then taken out, washed with distilled water, dried, and again weighed. It was found that the cathode had gained about $1{\cdot}2^{mgm}$ and the anode lost about $0{\cdot}4^{mgm}$.

It had been found throughout these experiments that the negative charge was not as effective as the positive, which is perhaps due principally to its wasting faster than the positive. However, having four Leyden jars connected to the disk so as to hold the charge longer, I found the negative charge the more effective, and the direction of the deflection would often be reversed at the first observation taken after charging. The first observation was not generally taken until about 10 minutes after charging so as to allow the induction to disappear. Having reversed the direction with a negative charge, the jars were discharged. Now leaving everything as before but

charging the jars positive, the direction of the deflection was again reversed.

The experiments were repeated with pure zinc amalgamated electrodes in zinc sulphate with the same results. The zinc cell did not, generally, give as large a deflection as the copper and so could more easily be reversed.

The greater effectiveness of the negative charge when it is sufficiently large may be due to the fact that the positive ions move faster than the negative, and the attracted ions would be guided more effectively than the repelled.

Toward the close of this work the humid weather interfered with the experiments somewhat, but results were obtained which indicated that it would be possible to entirely waste away the anode, by letting the electrostatic charge act on the closed circuit for a sufficiently long time.

It was intended also to test a non-electrolyte by this method, using a sugar solution, but the distilled water I was able to obtain always gave a deflection in the galvanometer, showing that it contained some dissociated electrolyte, and therefore this test could not be made.

These experiments have shown :—

1. That, when a cell containing an electrolyte is connected to a Daniell, although the electromotive force is below the decomposition value of the electrolyte, the solution in the neighborhood of the anode becomes positive, or in the neighborhood of the cathode becomes negative, or both.

2. That, after an electrolyte has been electrolyzed by a current, it is affected by an electrostatic charge in such a way that the liquid nearest the charge becomes of the opposite sign, or the liquid farthest from the charge becomes of the same sign as the charge, or both.

That is, an electrolyte after having been electrolyzed acts as if it contained particles charged with electricity which are free to move and may be directed by an electrostatic charge.

3. That an electrolyte subjected to an electromotive force less than the decomposition value of the solution behaves in a similar manner.

4. Finally, that an electrolyte which has never been acted upon by a current also behaves in a similar manner when acted upon by an electrostatic charge.

That is, it behaves as if it contained particles charged with electricity, which are free to move, and these particles have not been produced by a current.

This corresponds to the definition of free ions.

In conclusion I wish to thank Professor Wright, who suggested the subject and a large number of the experiments, and whose advice and assistance has always been cheerfully given.

Sloane Physical Laboratory, New Haven, June, 1902.

Art. XXX.—*On the Solution of Problems in Crystallography by Means of Graphical Methods, based upon Spherical and Plane Trigonometry;* by S. L. Penfield.

Introduction.—It is believed that all who have occasion to teach mathematical crystallography must have had experiences similar to those of the present writer. There are occasional students who find the subject very easy. These are naturally persons who are proficient in mathematics, and have good imaginative powers and a quick eye for grasping geometric forms. A little guidance from the instructor and some experience in handling crystals and apparatus are all that such persons require in order to obtain a very satisfactory grasp of the subject. The majority of students, however, find the subject somewhat difficult, one of the chief reasons for this being that they are troubled by the mathematics, although the latter embraces, for the most part, only simple principles of geometry and spherical and plain trigonometry. Probably the majority of those who undertake the study of crystallography are especially interested in the subject because of its practical bearings on chemistry, mineralogy and petrography. They are not especially mathematical in their tastes, and the calculations needed for the solution of the numerous problems which arise seem difficult and distasteful, not so much because of want of suitable training, but because, in all probability, mathematical principles have not been used very much in their other studies, perhaps, for a number of years; hence it is that innumerable difficulties and discouraging mistakes are often encountered when numerical calculations are made by means of formulas and logarithms. Probably all crystallographers have found numerical calculations burdensome, and the only real way to absolutely avoid mistakes is either to do all work in duplicate, or to apply some other method of checking results. The main object of the present communication is to set forth and explain certain graphical methods, based chiefly upon the stereographic projection, which have been found very useful in the writer's laboratory, and it is believed that they are especially applicable not only for the presentation of crystallography to beginners, but also for the solution of many complicated problems which may arise.

All who have worked much at crystallography have doubtless made use of graphical methods to a greater or less extent, and many descriptions of such methods may be found, but for the purposes of the present communication it does not seem necessary to review the work already done by others, as

the methods to be presented, though based on simple principles, are worked out, for the most part, along lines differing from those generally recommended. The principles involved in solving problems in spherical trigonometry by graphical methods have been already fully explained by the present writer in a communication entitled, "*The Stereographic Projection and its Possibilities from a Graphical Standpoint*," * to which frequent reference will be made. The advantages of the methods there described are that the mathematical principles involved may be comprehended easily, and only a simple and inexpensive outfit is needed for carrying on the work. With a little study, the methods may be mastered by any one, whether well equipped in mathematics or not, and for the solution of most problems the results are sufficiently exact. Whenever numerical calculations must be made, the processes of solving the problems graphically furnish the key to the methods of making needed calculations.

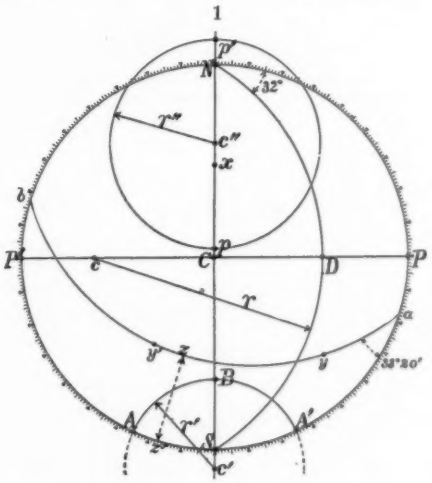
From an educational standpoint it is always a gain to do things understandingly, rather than mechanically, and the advantages of the graphical methods about to be described are that approximate solutions of all kinds of problems in crystallography may be made quickly without the use of tables or formulas of any kind, while at the same time an accurate and useful projection, or map, has been constructed.

In the actual study of crystals, after having made all necessary measurements and determined the system of crystallization, three processes must generally be followed: (1) The determination of the symbols of the several forms observed. (2) The determination of the axial ratio from certain selected *fundamental measurements*. (3) The calculations of a number of interfacial angles from the fundamental measurements. For the first of these processes graphical methods are quite sufficient, especially when it is borne in mind that, owing to the numerous imperfections of crystals, the best measurements which may be had are at times only approximately near the truth. The two remaining processes must be carried out by means of numerical calculations, unless the methods suggested by Fedorow† are employed, but the graphical methods, if likewise followed out, will furnish a ready means of checking numerical work. It may also be pointed out that as examples multiply of minerals and other chemical compounds whose crystallographic properties have been carefully studied, it becomes less often necessary to make calculations; for the work on any compound, when once well

* This Journal (4) xi, pp. 1–24 and 115–144, 1901.
† Zeitschr. für Kryst., xxxii, 464, 1890.

done and recorded in the literature, need not be repeated. Hence a student of crystallography, working as would naturally be the case, on well-known compounds, may be able to solve the majority of the problems presented for study by means of graphical methods, and thus be spared much of the time-consuming labor of making numerical calculations.

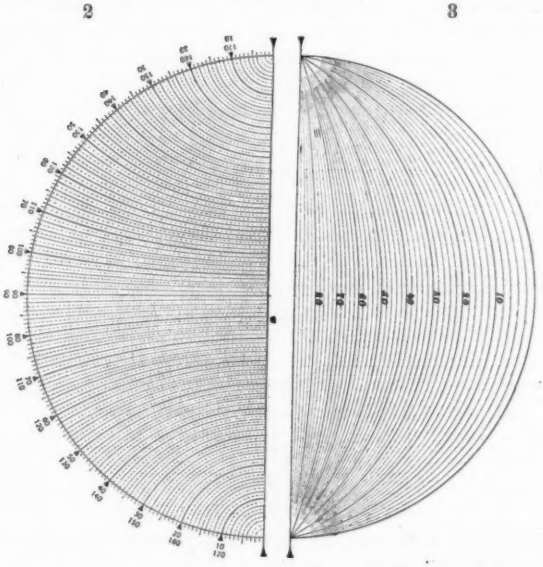
Outfit.—For executing the graphical methods described in this paper the following articles are needed: (1) Paper upon which a graduated circle and certain stereographic scales have been printed. (2) Stereographic protractors for plotting and measuring. (3) Beam-compass. (4) Curved ruler. (5)



Two triangles and a set of drawing instruments, including a needle-point and hard pencils.

The uses of most of the above-mentioned appliances have already been described, and only a few suggestions concerning them are now needed. The paper mentioned has a circle of 14^{cm} diameter, graduated to degrees, printed on it, the circle shown in figure 1 being a reduced copy. Four scales, of which frequent use will be made, are also printed on the paper. No. 1 gives the lengths of radii for describing arcs of great circles; for example, if it is known that the point D, figure 1, is 32° from P, the radius r for describing the great circle NDS may be taken directly from the scale. Scale No. 2 gives the lengths of radii for describing ares of small circles about points which are located on the divided circle; for example, it being known that the point B, figure 1, is 25° from S, and

through B a small circle ABA' is to be drawn, every point of which is 25° from S, the radius r' is given by the scale. On a sphere, the center for describing such a circle would be at S; in the stereographic projection, however, the center c' lies beyond S, on the diameter NS. Scale No. 3 is a stereographic scale, giving the distance in degrees from the center C to any desired point; for example, in figure 1, to the point x, which is 51° from C. About x a small circle has been drawn, every point of which is 46° from x. By means of scale No. 3 the needed points were located; x, 51°; p, 5°=51°—46°; and p',



97°=51°+46°, all measured from C; and the radius r'' for describing the circle is half the distance from p to p', the center c'' falling somewhat beyond x. Scale No. 4 gives decimal parts of the radius of the divided circle, and is used for measuring the lengths of axes, assuming the radius of the circle as unity.

The stereographic protractors needed are three in number. One of these (referred to as protractor No. I and shown in figure 4 of the former article) is printed on cardboard, and has along its base line a graduation which will be referred to in this paper as the *stereographic scale*. The scale is the same as a portion of that designated as No. 3 on the drawing paper; hence this protractor is not essential, but its convenience will

recommend it. The second protractor, figure 2, is a measuring scale, consisting of a series of stereographically projected small circles drawn about the 0° and 180° points. It was described in the former paper as protractor No. II, having a circular form, but one-half of the circle, which is superfluous, has since been cut away from the original plate. It will be referred to in this paper as the *small circle protractor*. The third protractor, figure 3, consists of a series of stereographically projected great circles, and will be referred to as the *great circle protractor*. Purposely no numbers are printed on this protractor, and those using it will do well to lay it printed side down and number the graduation with India ink, as shown in figure 3. If a number then happens to interfere with the uses of the protractor, it may be easily washed away. The uses of the protractors may be explained by reference to figure 1. If y and y' are two points on a stereographic pro-

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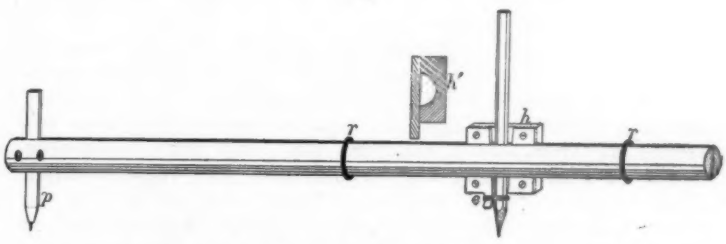

jection, the great circle passing through them may be found by centering the great circle protractor, figure 3, over the projection and turning it until an arc is found which passes through, or proportionately near, y and y'. The position of the protractor then determines the points a and b on the periphery, and its graduation gives the angle at a, 33° 20′, or the distance z to z'. Knowing the distance z to z', the radius for constructing the great circle may be taken directly from scale No. 1 of the drawing paper. By now applying the small circle protractor, figure 2, with its 0° and 180° points at a and b, the distances a to y and a to y' may be determined from the graduation, and the difference gives the distance y to y'. Thus a great variety of measurements may be made with facility and rather astonishing accuracy.

A beam-compass is an essential for accurate work, as ordinary dividers are not stiff enough to be relied upon for drawing circles having long radii. A compass constructed on the principles shown in figure 4 may be recommended, the idea having been suggested by Professor Charles B. Richards of the

Engineering Department of the Sheffield Scientific School. The beam is constructed from a round stick of hard wood, ¾ inch diameter, sawed lengthwise. The needle-point *p* is prepared by gluing the surfaces of two pieces of hard wood, placing a needle between them and pressing in a vise. After hardening of the glue, the piece is trimmed down to convenient size, and is held firmly in place between the half-rounds by means of two screws. Two rings *r* and *r* (obtained from a harness shop) serve to grip the pencil firmly between the two sticks. The block *h* is not essential, serving simply to hold the pencil (fastened by an elastic at *e*) when its position is shifted. A fine adjustment is had by moving the upper end of the pencil, which gives a much slower motion to the point. In order to adjust the pencil quickly with reference to scales 1 and 2 of the drawing paper, it is convenient to have these scales pasted on the beam. The writer has found compasses of this description most convenient, and rather prefers them to the beam-compasses listed by dealers in drawing instruments at a rather high price.

A curved ruler is indispensable for drawing some very flat circular arcs. The form first suggested by Wulff* and modified by the present writer† is recommended. The ordinary drawing instruments need no especial comment. Two triangles of transparent celluloid (45° and 60°), measuring about 12 inches along the hypothenuse, are recommended. Their edges serve as rulers, and when held one against the other, the edge of the farther triangle being set at any desired angle, the direction may be transferred to any point by sliding the farther triangle along the edge of the near one, held firmly against the drawing paper.

As the scale upon which the plotting is done is rather small, a lens is recommended, and it is especially convenient to have one mounted on a stand. The kind suggested by the writer, and shown in figure 33 of his earlier paper, though expensive, has proved most useful.

Having described the necessary outfit, attention may next be directed to consideration of the principles upon which the methods of plotting are based.

The Spherical Projection.—The stereographic is often called the *spherical projection*, but it is believed that it would be best to restrict the use of the latter term, in so far as it concerns crystallography, to the projection of the faces of a crystal upon a sphere. This latter conception is a very simple one: A crystal is supposed to be located at the center of a sphere,

* Zeitschr. für Kryst., xxi, p. 253, 1892.

† The Stereographic Projection and its Possibilities, loc. cit., p. 138.

figure 5, its vertical axis orientated so that it corresponds with the axis joining the north and south poles; then from the center of the sphere lines, *normals* are supposed to extend out, at right angles to the several crystal faces, until they touch the surface of the sphere, where they locate points, known as the *poles* of the faces. Figure 5 was plotted with much care in clinographic projection, and was made partly with the idea of putting on record a good figure illustrating the simple principles of the spherical projection. A combination of cube *a*, octahedron *o*, and dodecahedron *d* is shown, with normals extending to the surface of an imaginary sphere. The projected

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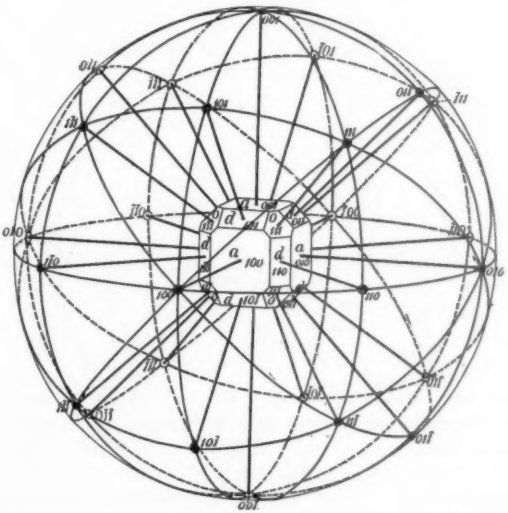

great circles, uniting the poles of the faces, are shown in the figure as ellipses. The figure well illustrates the important principle, that the normals to a series of faces which are in a zone all lie in one plane, and touch the sphere on an arc of a great circle. The length of arc between the poles of any two faces, as measured on a great circle, is the same as the angle between the normals, hence the same as between the faces as measured with the reflection goniometer. Wire models constructed on the principles shown in figure 5 are very helpful to beginners.

For studying crystals, it is convenient to make use of the stereographic projection. Generally the poles of one hemisphere only (the upper) are represented, the projection being made on the horizontal plane, or plane of the equator. The

point of vision is then at the south pole, $00\bar{1}$, of figure 5. A model, similar to one made by the writer and illustrated in an article on Map Projection,* is a help in conveying to beginners correct ideas of the principles upon which the stereographic projection is based.

The fundamental proposition of mathematical crystallography.—That property which must first be ascertained for every crystallized substance is its system of crystallization, and then follow the determinations of the inclinations and lengths of the axes. Figure 6 represents a general proposition (the axes shown are those of rhodonite, triclinice) in which the quantities sought are the axial inclinations α, β and γ, and the lengths of the axes a and c, it being assumed that b is equal to unity. The angles α, π and ρ of figure 6 are those of a plane triangle with the axes b and c for its sides, and it is evident that after having determined α (the b axis being unity) it is

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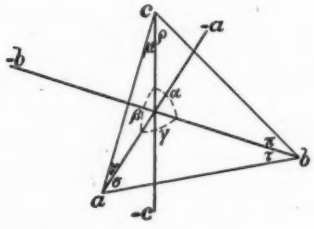

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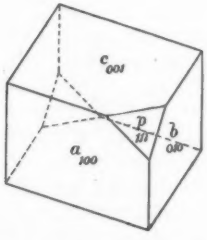

only necessary to find either π or ρ in order to solve the triangle and obtain the length of the c axis. Likewise, γ having been determined, it is only necessary to find either τ or σ in order to obtain the length of the a axis. With β and the length of one axis, either a or c, determined, the length of the other axis may be found if either μ or ν is known. For the complete solution of a problem in the triclinic system, therefore, the axial inclinations α, β and γ must be determined, and in addition only two other angles are needed (τ and π, for example) in order to find the lengths of a and c. As will be shown, all of the desired parts α, π and ρ; γ, σ and τ; and β, μ and ν are to be found on a stereographic projection, where angles are preserved so that they may be measured.

Figure 7 represents a hypothetical case, a combination of the three pinacoids a, 100; b, 010; and c, 001 of rhodonite, in combination with the pyramid p, 111. Five measurements made on such a crystal suffice for the solution of the problem, and for rhodonite they may be as follows:

* This Journal, xiii, p. 247, 1902.

$a \wedge b$, $100 \wedge 010 = 94° 26'$ $\quad a \wedge p$, $100 \wedge 111 = 56° 19'$
$a \wedge c$, $100 \wedge 001 = 72 \ 36\frac{1}{2}$ $\quad c \wedge p$, $001 \wedge 111 = 29 \ 49$
$b \wedge c$, $010 \wedge 001 = 78 \ 42\frac{1}{2}$

The lengths and inclinations of the axes derived from the foregoing measurements are as follows:

$$a : b : c = 1{\cdot}07285 : 1 : 0{\cdot}62127;$$
$$\alpha = 103° 18'; \quad \beta = 108° 44'; \quad \gamma = 81° 39'$$

From the measurements given above the poles a, b, c and p of rhodonite have been accurately located in the stereographic projection, figure 8, and through the poles the principal zones, corresponding to those of figure 5, have been drawn. The

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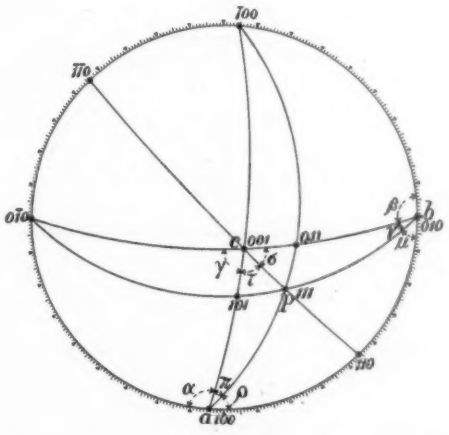

relation between figures 6 and 8 is a most important one. The angles a, π and ρ, made by the meeting of the great circles at the pole a, figure 8, are identical with a, π and ρ of figure 6, and a like correspondence holds true at the poles b and c of figure 8, as indicated by similarity in the lettering. In order to make clear that the angles a, π and ρ of the stereographic projection, figure 8, are identical with a, π and ρ of the rhodonite axes, which, it must be remembered, are shown in clinographic projection in figure 6 and therefore somewhat distorted, let it be assumed that a model corresponding to figure 5, but constructed so as to represent the triclinic system, is at hand. Since the front pinacoid a of figure 7 is parallel to the b and c axes, its normal is at right angles to the plane of these axes; hence if we imagine ourselves as looking at the b and c axes of a triclinic crystal in the direction of the normal to the

face *a*, 100 (the axes being properly orientated within a sphere, and the latter standing sufficiently far away to give the effect of orthographic projection), the relations shown in figure 9 would be seen. The outer circle represents the bounding surface of the imaginary sphere. The *b* and *c* axes are seen within the sphere with their true inclination and lengths; $a = 103° 18'$, and $b : c = 1.00 : 0.621$. Normals to all crystal faces parallel to the *c* axis (compare figure 5) are located in a plane at right angles to the *c* axis, which plane would be foreshortened in orthographic projection to the line *CC'*. Likewise normals to all faces parallel to the *b* axis lie in the plane represented by the line *BB'*. Since the planes represented in figure 9 by *CC'* and *BB'* are at right angles, respectively, to

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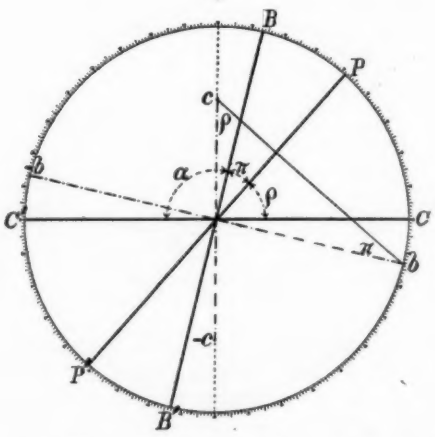

the *c* and *b* axes, they must make with one another an angle equal to that of the axes, that is *a*. All forms intersecting the *b* and *c* axes at their unit lengths, therefore, having the direction of their intersections represented by the line *bc*, figure 9, would have their normals in a plane at right angles to the direction *bc*. This plane seen in orthographic projection is represented by the line *PP'*, and, therefore, owing to the construction, the planes *BB'* and *PP'* make with one another an angle equal to π. In like manner the planes *CC'* and *PP'* make with one another an angle equal to ρ. Hence it is that the angles made by the planes in which the normals are located, represented by *CC'*, *BB'* and *PP'* in figure 9, are to be found in the stereographic projection, figure 8, at *a*, a line from *a* to the center of the sphere being the common intersection edge of the three planes. In like manner it may be demonstrated

that at the poles b and c, figure 8, where normals to the pinacoid 010 and the base 001 meet the sphere, the plane angles β, μ and ν and γ, σ and τ of figure 6 are to be found. How these facts are to be made use of, will subsequently be shown by examples.

Another principle which may be made use of for the solution of many problems is that based upon the conditions established by three faces in a zone, known by some as the cotangent and tangent relation.* For the purpose of illustrating this principle, reference is made to figure 10, which represents a regular arrangement of dots conditioning angles like those

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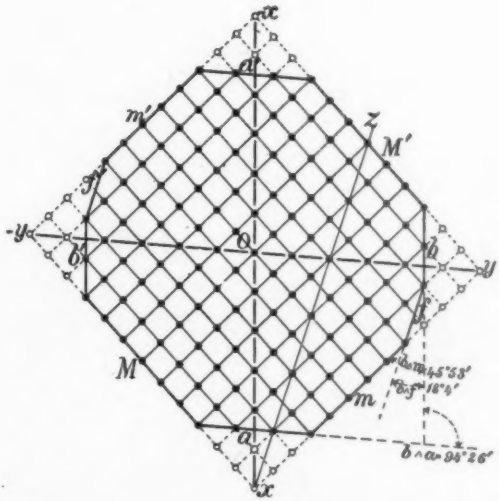

found in the prismatic zone of crystals of rhodonite. The dots may be regarded as representing crystal particles or molecules, and the forms shown by the heavy outline of the figure are the planes a (100), b (010), m (110), M (1$\bar{1}$0) and f (1$\bar{3}$0), as seen in orthographic projection. It may be assumed that the crystal is made up of layer upon layer of particles like the one shown, figure 10 being an orthographic projection of such a system of particles, as seen in the direction of the vertical axis of the crystal. Since rhodonite is triclinic, a single layer of particles, represented by the dots, does not lie in a plane parallel to the paper, but in a plane tilled down to the front and right by an amount indicated by the axial inclinations

*Dana's Text Book of Mineralogy, edition of 1898, p. 31.

$\beta = 108° 44'$, and $a = 103° 18'$. The lines x, $-x$ and y, $-y$, therefore, are not the true crystallographic a and b axes, but the somewhat foreshortened orthographic projections of the axes. Notwithstanding foreshortening, however, for all purposes of calculation in the zone under consideration, the lines $x,-x$ and $y,-y$ are *lines of reference*, regarding which the law of definite mathematical ratio of crystal faces holds true, the same as for real crystallographic axes. The angle between $x,-x$ and $y,-y$ is determined by the measurement of b (010) on a (100), and the angles of a third form, m (110), establishes the relative lengths of the lines of reference Ox and Oy. Any fourth face in the zone, therefore, when referred to Ox and Oy must have an inclination in conformity with the fundamental

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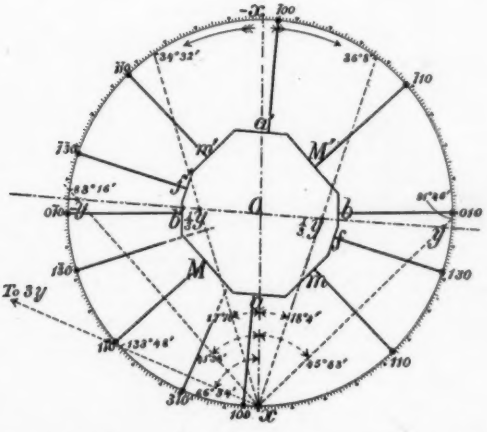


law of definite mathematical ratio. For example, in figure 10 the face f is parallel to the line $x\,z$ which intersects the line of reference Oy at one-third its length; the symbol of f is therefore 130, and the angle $b \wedge f$ is wholly dependent upon the two angles $b \wedge a$ and $b \wedge m$. Hence it is, that knowing the symbols and angles of three faces in a zone, the angle of a fourth face may be found if its symbol is given, or its symbol may be determined if its angle is given.

Figure 10 furnishes a key to the solution of problems like the one just given. Let it be assumed that on a rhodonite crystal two angles have been measured, as follows: $b \wedge a = 94° 26'$ and $b \wedge m = 45° 53'$, and that the poles 010, 100 and 110 are plotted on a divided circle, figure 11. Lines of reference $x,-x$ and $y,-y$ are then drawn through the center, parallel, respectively, to the b and a faces, therefore intersect-

ing the divided circle at 90° from the poles 010 and 100. A line parallel to the face *m* (at right angles to the normal to *m*) is next drawn. To do this easily use may be made of the principle of geometry that the angle between two lines meeting at the circumference of a circle is measured by half the arc intercepted on the periphery; hence the line may be drawn from *x* to 91° 46′ (twice $b \wedge m$, 45° 53′) on the graduation of the divided circle, measured from $-x$. This line determines a point *y* on the second line of reference, and establishes the ratio of *Ox* to *Oy*, the numerical value of which, however, need not be determined. Designating the distances *Ox* and *Oy* as *x* and *y*, respectively, the law of definite mathematical ratio demands that all faces in the zone under consideration must intercept the two lines of reference at definite multiples or fractions of *x* and *y*. In figure 11 the angle of $b \wedge f$ is 18° 4′, and by drawing a line from *x* to 36° 8′ (double the angle) on the periphery it is found that it intersects at $\frac{1}{3}\,y$; the symbol of the face is therefore 130. Likewise by drawing lines from *x* to $-\frac{1}{3}\,y$, $-y$, and $-3\,y$, the angles of the forms $1\bar{3}0$, $1\bar{1}0$ and $3\bar{1}0$ (measured from $0\bar{1}0$) are found, the values being most easily obtained by halving the arcs intercepted on the periphery, as indicated in the figure. The case just cited, although a simple one, is general, for it is wholly a matter of choice in the orientation of a rhodonite crystal that the forms designated as *b*, *f*, *m*, *a*, etc. are taken as parallel to the vertical axis.

Cases may arise where reliable measurements may be had from three known forms, for example, *b*, *f* and *m*, figure 11, and it is desired to find the angle of a fourth form *a*, 100, which may either be absent, or be of such poor quality as to yield no satisfactory measurement. To solve such a problem construct the line $x, -x$ parallel to *b*, and from *x* draw lines parallel to *f* and *m*. The direction of *a* is then found by constructing a line through the center which will be intersected by the lines previously drawn in the ratio $\frac{1}{3} : 1$. With the aid of a straight edge and a pair of dividers such a line is easily found.

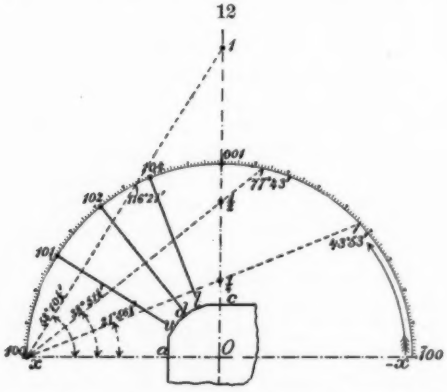
Again, it will often happen that the zone under consideration is of such a nature that the ratio of the intercepts on the line of reference *Oy* can not be told by simple inspection, in which case the following procedure may be resorted to. Any four faces taken in succession may be designated as *A*, *B*, *C* and *D*, and their indices, respectively, as *hkl*; *mno*; *pqr*, and *xyz*. Taking the first line of reference (corresponding to $x, -x$, figure 11) as parallel to the face *A*, the ratio of the intercepts on a line parallel to the fourth face *D* may be found from a system of left to right, right to left, cross-multiplica-

tion and subtraction, carried out according to the following scheme :*

$$\begin{array}{l} A,\ hkl \\ B,\ mno \\ B,\ mno \\ D,\ xyz \end{array} \quad \begin{array}{c} 1-2 \\ \hline hn-km \\ my-nx \end{array} ; \quad \begin{array}{c} 1-3 \\ \hline ho-lm \\ mz-ox \end{array} ; \quad \begin{array}{c} 2-3 \\ \hline ko-ln \\ nz-oy \end{array}$$

$$\begin{array}{l} D,\ xyz \\ C,\ pqr \\ C,\ pqr \\ A,\ hkl \end{array} \quad \begin{array}{c} xq-yp \\ \hline pk-qh \end{array} ; \quad \begin{array}{c} xr-zp \\ \hline pl-rh \end{array} ; \quad \begin{array}{c} yr-zq \\ \hline ql-rk \end{array}$$

The result of multiplying one of the upper expressions by that directly beneath gives the desired intercept. The result



in some cases is indeterminate, as, for example, schemes 1−3 and 2−3 applied to prismatic zones, where the third index of the forms is zero, or scheme 1−2 applied to a zone between some prism and base, where the first and second indices of the forms maintain the same ratio. When a numerical solution is desired the following equation is generally made use of:

$$\frac{\text{Cot } AC - \text{cot } AD}{\text{Cot } AB - \text{cot } AD} = \text{rational intercept.}$$

Provided AD equals 90°, its cotangent equals zero, and the problem is then much simplified. It may then be easier to

* Note.—The scheme of cross-multiplication and subtraction here suggested is essentially like that given in Dana's Text Book of Mineralogy, page 31, Groth's Physikalische Krystallographie, page 584, and other works, but by adopting, as has been done, a somewhat more symmetrical arrangement and procedure, the operation is more easily remembered and carried out.

consider the relation in terms of tangents rather than cotangents. The tangent principle, though simple, is so exceedingly important that it is thought best to introduce an example indicating a graphical method of solution. The illustration, figure 12, is chosen from barite, the forms shown being those of the macrodome zone, with $c=001$, and $a=100$. It is assumed that the angles have been measured as follows: $c \wedge l = 21°\ 56\frac{1}{2}'$; $c \wedge d = 38°\ 51\frac{1}{2}'$, and $c \wedge u = 58°\ 10\frac{1}{2}'$. The poles are easily located on the graduated circle, and the slopes of the several faces plotted by drawing lines from x to points on the periphery equal to twice the value of the angles, measured from $-x$. It is then evident that if u is taken as the unit dome 101, the intercepts of d and l on the vertical axis are respectively $\frac{1}{2}$ and $\frac{1}{4}$, and their symbols therefore 102 and 104. If the length of the a axis of barite were known ($a=0{\cdot}815$), the slopes of u, d and l would naturally be plotted from the unit length of a, when the slope of u

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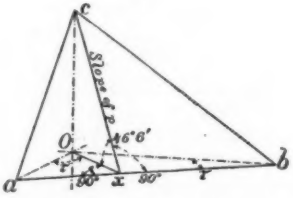

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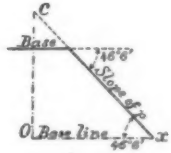

would determine the length of the vertical axis ($c=1{\cdot}314$). For plotting and measuring the lengths of axes, the radius of the divided circle may be taken as *unity*, and measurements of axial lengths made by means of scale No. 4 of the sheets on which the divided circles are printed.

Another procedure applicable to all cases where the axial inclinations are 90° is illustrated by figures 13, 14 and 15. In figure 13 three axes meeting at 90° at O, and their intersections with a pyramid *abc*, are shown in clinographic projection. The line Ox, at right angles both to the vertical axis and the edge *ab*, is an important factor to consider, and may be designated as the *base-line* of the triangle cOx. Another important factor to be considered is the slope of the pyramid, or its inclination, along the line xc, with the base-line Ox. From figure 14, which represents a section along the plane cOx of figure 13, it may be seen that the slope of a pyramid, or the angle made by the line cx with the *base line* Ox, is the same as the interfacial angle of base on pyramid, 46° 6′ in the figure. Knowing the *base-line* Ox and the slope of any pyramid, there-

fore, the problem may be plotted to scale and the length of the vertical axis Oc determined. The foregoing simple trigonometric relations may now be applied to figure 15, where the divided circle is employed for the double purpose of a stereographic projection and for solving problems in plane trigonometry. Let it be supposed that the poles of the three pinacoids 100, 010 and 001, and of a pyramid p have been accurately located in stereographic projection. Through 001 and p a line is drawn which is the projection of a great circle (a meridian) determining the point m on the divided circle. Since the axial inclinations are 90°, the value of τ (compare figures 6 and 8) is measured by the arc $100 \wedge m$, which in figure 15 is 39° 11′. Considering the radius of the divided circle as *unity*

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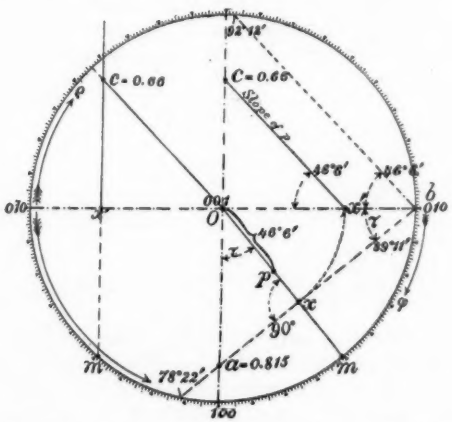

and as equal to the b axis, the tangent of τ ($100 \wedge m$) gives the intercept on the a axis; accordingly this may be found by drawing a chord from 010 to a point on the divided circle equal to twice $100 \wedge m$, measured from $0\bar{1}0$. Applying scale No. 4 of the printed sheets along the direction of the a axis, the length of the axis is found to be 0·815. The chord ba, figure 15, determines also the point x on the radius passing through p, and the distance from x to the center is the *base-line* corresponding to Ox of figures 13 and 14. The numerical value of the length of the *base-line*, which is equal to the sine of τ, need not be determined, but the distance may be transposed to x' on the horizontal line by means of dividers. Applying the stereographic scale to the radius passing through p, the angle of $001 \wedge p$ (the slope of the pyramid) may be measured, equal to 46° 6′ in figure 15, and a line drawn at this

angle from x' intersects the vertical line at a point c, which, when measured with scale No. 4 of the printed sheets, gives the length of the vertical axis, $c=0{\cdot}66$. The whole procedure of determining the lengths of the a and the c axes is exceedingly simple both in its principles and in its execution, and with slight modifications may be applied even to the monoclinic system where the b axis is at right angles to the a and c axes.

Instead of laying off the *base-line* Ox' to the right of the center by means of dividers, as shown in figure 15, it may be plotted to the left, by making use of the principle that Ox equals the sine of τ. Accordingly locate m to the left on the divided circle, and draw a vertical chord; then plot the slope of p from the center, making use of the graduation of the divided circle, and measure the length of the vertical axis on the chord $x'c$. On one divided circle, therefore, a stereographic projection may be made in three quadrants, reserving the upper left hand quadrant for plotting the length of the vertical axis. It may be noted that almost at a glance at such a chart the two important angles of the two-circle goniometer, φ and ρ, may be told from the graduation; for example, the radius through p, figure 15, determines m, and, therefore, the angle φ, measured from 010, which is nearly 51° in figure 15; and the slope of p, plotted from the center and intersecting the vertical chord at 0·66, meets the divided circle at a little over 46°, which is the angle ρ, measured from 010. For plotting measurements made with the two-circle goniometer and interpreting the results, the method is most admirably adapted.

Having explained at considerable length the principles involved in solving problems graphically, some examples of the application of the methods to specific problems in the several crystal systems will next be given. The examples cited are problems which have been encountered in the writer's laboratory, and in all cases it will be assumed that the fundamental measurements were made to the nearest minute, hence the results of plotting will indicate the accuracy of the graphical methods. Generally, the scheme indicated in figure 15 will be followed, that is, the stereographic projection will be made on the lower half of the divided circles, reserving the upper half, or the upper left hand quadrant, for plotting the intercepts on the vertical axis. The horizontal radius, from the center to the right, will indicate the b axis and the lower radius the a axis. *Base-lines* corresponding to Ox of figures 13, 14 and 15 will be transposed to the horizontal diameter, as in figure 15, and indicated by correspondence in lettering. The graphical solutions were all executed carefully with fine pencil lines and

subsequently traced with India-ink in order to adapt the work to photo-engraving. The illustrations, therefore, are all from the original sheets on which the plotting was done.

Isometric System.

In this system the axes are of equal lengths, and it is necessary to determine from measured angles the symbols of the forms, or, having the symbols given, to find the interfacial angles. The first problem that will be presented is one which might, for example, be given to a beginner for the purpose of introducing the subject of mathematical crystallography and showing the relations between crystal forms and their angles. It may be supposed that the student is supplied either with models or crystals from which measurements are derived.

Starting with a simple combination, the poles of the cube are first located at 100, 010 and 001, figure 16, and those of the dodecahedron at distances of 45°, midway between them, the positions of 101 and 011 being determined by the stereographic scale. By means of the small circle protractor it may now be found that the distances between the poles of the dodecahedron are 60°. The octahedron truncates the solid angles of a cube, and is in the zones between cube and dodecahedron (compare figure 5); its poles may therefore be located by drawing the necessary great circles. The pole 111 being thus located, it may be found by the stereographic scale that the distance from 001 to 111 is $54\frac{3}{4}°$, theory 54° 44′, and from 111 to 110 is $35\frac{1}{4}°$, while like results will be obtained by measuring from 100 or 010 with the small circle protractor. Thus a conception is quickly gained, not only of the relations of the important forms, cube, octahedron and dodecahedron, but also of the values of their interfacial angles.

For simplicity of plotting, the tetrahexahedron is the next best form to consider, and a fluorite crystal with bevelled edges may be chosen as an example for study. The angle of one of the bevelling face to cube is 18° 26′, and the poles appear on the stereographic projection in the zones between cube and dodecahedron. To determine the symbol of one of the poles, for example, 310, figure 16, it is only necessary to note the distance from 100 (18° 26′) and draw a line from 010 making the same angle with the diameter, which line intersects the front axis (radius) at $\frac{1}{3}$; the ratio on the first and second axes is therefore $\frac{1}{3}\,a : a$, and the indices of the pole are 310. The interfacial angle of the tetrahexahedron, the distance from 310 to 301, measured with the small circle protractor, was found to be 25° 50′, theory 25° 50′.

The trisoctahedron bevels the edges of an octahedron; its poles, therefore, are always to be found on the zones between octahedron and dodecahedron. Taking a crystal of galena, an octahedron with bevelled edges, as an example, the angle of the trisoctahedron, measured over an octahedral edge, is 38° 56′. One-half of the foregoing angle, 19° 28′, is therefore that of trisoctahedron on dodecahedron, and the pole between 110 and 111 is easily located by means of the stereographic scale. To determine the symbol of the form, which, being in the zone between 110 and 111, must have a 1 : 1 relation on the first

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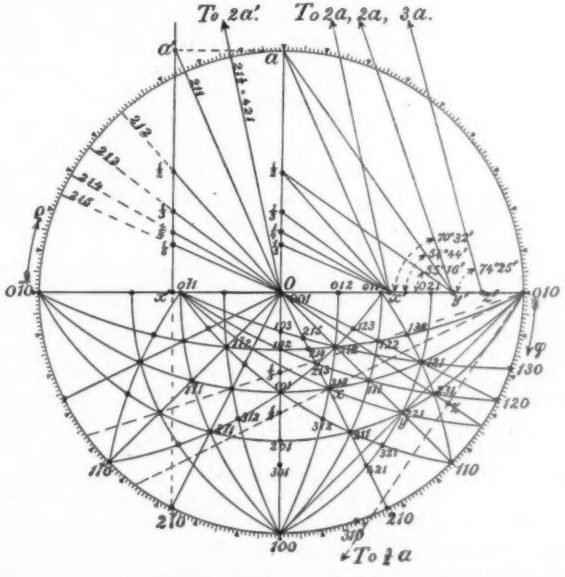


and second axes, draw the line from 010 to 100 and thus determine the base-line *Oy*. The slope of the face, its angle on 001, is 70° 32′ (complement of 19° 28′), hence from *y'* (the base-line transposed to the horizontal diameter) construct a line at 70° 32′, which, if continued, will meet the vertical axis (radius) at 2*a*. The form intersects the axes, therefore, at *a* : *a* : 2*a*, the indices being 221. To fix the pole 212 between 111 and 101, place the small circle protractor over the projection, its zero at 010, and space off the distance 19° 28′ from 101 with dividers; then transpose to the paper. Another and better way is to lay off the distance 19° 28′ from 001 on the horizontal diameter, and construct a small circle with radius

70° 32′, taken from scale No. 2 of the printed sheets. To find the interfacial angle from 221 : 212, make use of the great circle protractor for finding the great circle between the poles, construct the great circle and measure with the small circle protractor as indicated on page 253. From 221 to 212 was found to be 27° 35′, and from 221 to 122, 27° 15′, the calculated distance being 27° 16′.

The poles of the trapezohedron are found on the great circles between octahedron and cube. With garnet as an example, measurement may be made over an axis, and the angle is 70° 32′, one-half of which is the angle of cube on trapezohedron. The pole between 001 and 111 may then be located by means of the stereographic scale, at 35° 16′ from 001, and the slope plotted from the base-line Oy' goes to $\frac{1}{2}$ on the vertical axis; the indices are therefore 112. By applying the great circle protractor it is found that 112 is in the zone of the dodecahedrons 101 and 011, and this relation may be made use of for locating other poles of the trapezohedron, 211 and 121. Other interfacial angles may then be measured; for example, $112 \wedge 1\bar{1}2$ and $211 \wedge 2\bar{1}1$ were found to be, respectively, 48° 30′ and 48° 10′, theory 48° 11′, and $211 \wedge 121$ and $121 \wedge 112$, 33° 45′ and 33° 15′, theory 33° 34′.

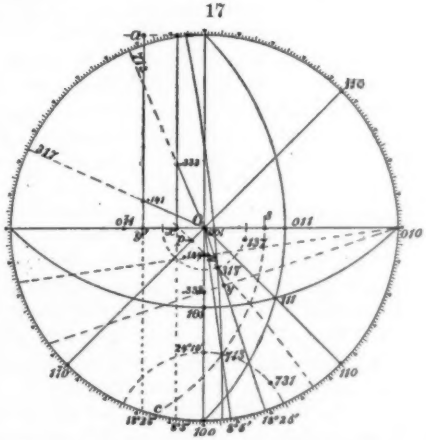
The hexoctahedron most frequently met with on garnet bevels the edges of the dodecahedron, the angle between the bevelling faces being 21° 47′, or 10° 54′ from the trapezohedrons. To locate the pole between 101 and 112, place the small circle protractor over the projection with its zero at $1\bar{1}0$, then with dividers space off 10° 54′ from 112 and transfer to the paper. A radius drawn through the point thus found intersects the divided circle at a little over 26½° from 100. A line from 010, drawn at right angles to this radius, intersects the first axis (radius) at $\frac{1}{2}$, and establishes the relation $\frac{1}{2}a : a$ on the first and second axes and also the base-line Ox. The distance from the hexoctahedron to 001, measured with the stereographic scale, was found to be just short of 37°, and this slope plotted from x' intersects the vertical radius at $\frac{1}{3}$. The form is therefore $\frac{1}{2}a : a : \frac{1}{3}a$, the indices being 213. The poles of the hexoctahedron under consideration are especially easy to locate by means of zones, as indicated in figure 16, and to show the accuracy with which the plotting was done some distances measured on the projection are given, as follows: $111 \wedge 231 = 22°\ 5'$, theory 22° 12′; $010 \wedge 231 = 36°\ 45'$, theory 36° 42′; $312 \wedge 3\bar{1}2 = 31°\ 10'$, theory 31° 00′; and $001 \wedge 231 = 74°\ 25'$, theory 74° 30′. The method of finding the symbol of the pole 231 ($\frac{3}{2}a : a : 3a$) by means of the base-line Oz and slope 74° 25′ is indicated in figure 16, but needs no discussion. Attention is called to the six poles in the zone

between 001 and 210, determined by the intersections of zones. Their distances from 001 being measured with the stereographic scale, the slopes may be plotted either from x' to the right or, better, from the center, and their intersections with the vertical radius, or the perpendicular erected at x' to the left, then determined. The distances from 001 to the several poles, measured with the stereographic scale, were found to be as follows:

Form	215	214	213	212	211	421
Measured,	24° 5′	29° 5′	36° 55′	48° 10′	66° 00′	77° 15′
Calculated,	24 5	29 12	36 42	48 11	65 54	77 23

Two methods for determining the symbol of a hexoctahedron, observed in combination with the cube on crystals of

17



fluorite from Weardale, Durham, England, are indicated by figure 17. No zones were encountered in measuring the crystal, hence two measurements were necessary for determining the form, those made being between two hexoctahedron faces adjoining a cube, 21° 13′, and from cube to hexoctahedron, 24° 19′. Starting from the center of a stereographic projection, the poles of eight faces of the hexoctahedron must lie on a small circle drawn about 001 with a radius of 24° 19′, which may be taken from the stereographic scale. Moreover, the poles of the hexoctahedron must lie symmetrically on either side of a radius passing through 111, distant 10° 36′ (half of 21° 13′) from the pole of a possible truncating face, or 79° 24′ (the complement of 10° 36′) from $1\bar{1}0$ and $\bar{1}10$; accordingly the point p was located at 10° 36′ from the center on the radius to $1\bar{1}0$, and, taking the radius 79° 24′ from scale No. 2 of the

sheets, a small circle through p was constructed which intersected the small circle previously drawn at the point marked 317. Through the point thus found a radius was drawn, which intersected the divided circle at 18° 25′, and from 010 a line at right angles to the radius was drawn, thus determining the intercept $\frac{1}{3}$ on the first axis, as also the base-line Oy. The angle of cube on hexoctahedron is 24° 19′, hence a line drawn from the center at this angle was found to meet the perpendicular from y' at 0·141, determined by scale No. 4 of the printed sheets, or practically $\frac{1}{7}$th of the radius, the true value being 0·143; hence the axial relation of the face under consideration is $\frac{1}{3}a : a : \frac{1}{7}a$, the indices being 317.

It is always an advantage to plot near the periphery of a stereographic projection, where the spaces between degrees are larger than near the center; therefore a solution, similar to the one just given, but made about 100, is also shown in figure 17. The small circle with radius 24° 19′, taken from scale No. 2, was first drawn about 100. All points on the zone 100 to 011 are 90° from 0$\bar{1}$1, hence the desired pole may be located by means of a small circle constructed about 0$\bar{1}$1 at a distance of 79° 24′. To do this, two points were located on the horizontal diameter at 79° 24′ from 0$\bar{1}$1, to the right and left, making use of scale No. 3 of the printed sheets. One of these points is at s, figure 17, the other too far to the left to be shown, and through them the small circle sc was constructed, which intersects the small circle previously drawn at the desired point, marked 713. To find the symbol, the radius through the pole 713, and the chord from 010 at right angles to it, were drawn; thus the intercept on the first axis was found to be 0·144 or $\frac{1}{7}$. By means of the stereographic scale the distance from 001 to the pole 713 was found to be 67°, and this angle plotted from the center intersects the perpendicular from x' at 0·333 or $\frac{1}{3}$. The axial relation is therefore $\frac{1}{7}a : a : \frac{1}{3}a$, the indices being 713. The distance from 713 to 317, measured with the small circle protractor, was found to be 43° 15′, theory 43° 13′.

Tetragonal System.

In this system the problem presents itself of finding from one fundamental measurement the length of the vertical axis, and from interfacial angles the symbols of occurring forms. The example chosen for illustration is a crystal of octahedrite from Brazil, given to the writer by Professor Groth of Munich. The crystal, shown in figure 18 in orthographic* and clino-

* The orthographic projection is represented as revolved 18° 26′ about the vertical axis, the reason for which will be explained in an article now in preparation.

graphic projection, was studied and figured by Mr. P. B. Condit.

The combination is a simple one, base $c(001)$, pyramid $p(111)$ and ditetragonal pyramid s. As fundamental measurement the angle of $p \wedge p$ over the base, 136° 36′, was chosen, from which $c \wedge p = 68°\ 18'$ is obtained. The poles of the pyramid p are easily located, figure 19, by means of the stereographic scale. Erecting a perpendicular at x' to represent the vertical axis, and plotting the angle 68° 18′ from the center, the length of the vertical axis was found by means of scale No. 4 to be

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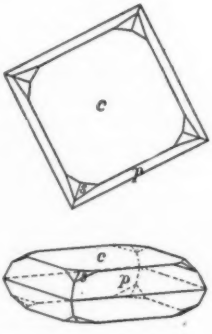

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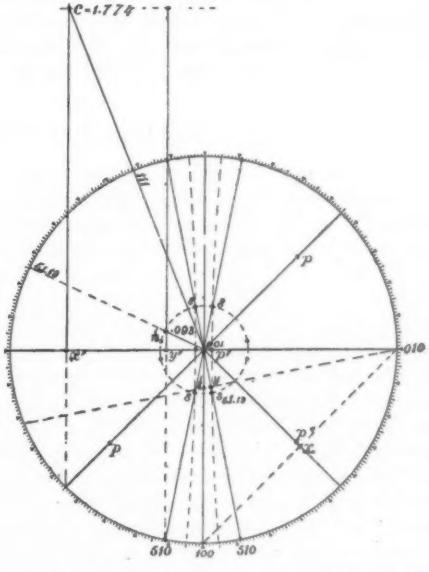

1·774, the calculated length being 1·777. By means of the small circle protractor the distances between the poles of the pyramid, $111 \wedge 1\bar{1}1$ and $111 \wedge \bar{1}11$ were found to be 82° 20′ and 82° 15′, the calculated value being 82° 9′.

For the determination of the symbol of the ditetragonal pyramid, the angles between two adjacent s faces and from c to s were measured, as follows: $s \wedge s = 9°\ 40'$, $c \wedge s = 25°\ 30'$. About the center a small circle with radius 25° 30′, taken from the stereographic scale, was first described, upon which the poles of the pyramid must be located. Since $s \wedge s$ is 9° 40′, four of the poles (those lettered s in figure 19) must be symmetrically located at 4° 50′ on either side of the vertical diam-

eter: accordingly p' was located at 4° 50′ from 001 on the horizontal diameter, and by means of the curved ruler a small circle was drawn through p' and points on the divided circle 4° 50′ from 100 and $\bar{1}00$. The intersections of the small circles shown in figure 19 locate the poles of four of the s faces. Through the poles thus found diameters were drawn, which were found to intersect the divided circle at about 11° 10′ from 100, and a chord from 010 at right angles to one of these diameters intersects the front axis (radius) at just a trifle short of 0·2, or $\frac{1}{5}$. The distance 100 to 510 by calculation is 11° 18′. Erecting a perpendicular at y' and plotting the angle $c \wedge s$, 25° 30′, from the center, the intersection on the perpendicular, measured with scale No. 4, was found to be 0·093 or $\frac{1}{19}$th of the vertical axis found, 1·774÷19=·0933. The relation of the s faces on the axes is therefore $\frac{1}{5}a : a : \frac{1}{19}c$, giving 5·1·19 as the indices.

Hexagonal System.

The example chosen for illustrating this system is a crystal of calcite from Egremont, England, shown in figure 20. The angle $r \wedge r$, 74° 55′, was selected as the fundamental measurement, and the poles of r were located as follows: Since $r \wedge r$ =74° 55′, $a \wedge r$, figure 21, must equal the complement of one-half $r \wedge r$, or 52° 32½′; accordingly, on the radii Oa_1 and $O-a_2$ the points s were located at 52° 32′, respectively, from a_1 and $-a_2$, and, using scale No. 2 of the printed sheets, small circles sc were drawn through the points s, which intersect at r. The distance Or, measured with the stereographic scale, was found to be 44° 40′, calculated 44° 37′. The inclination thus found, plotted from O, meets the perpendicular from x' at 0·854, calculated 0·854. Having located the poles r, the great circles uniting them were constructed. The two scalenohedrons v and ζ are in the principal zones of the rhombohedron, between r and a, and were located on the stereographic projection by the measurements $a \wedge v$=23° 31′ and $a \wedge \zeta$=10° 34′, the small circles $c's'$ and $c''s''$, respectively, 23° 31′ and 10° 34′ from $-a_3$, figure 21, serving the purpose. The radius through v and the chord from a_2 at right angles to it establish the relation on the horizontal axes, $\frac{1}{2}a : a - \frac{1}{8}a$, and also the length of the base-line Oy. The slope of the face, the distance Ov, measured with the stereographic protractor, was found to be 69° 00′, calculated 69° 2′, and this angle plotted from the center intersects the perpendicular from y' at just a trifle short of 0·854, or unity, the discrepancy being due to slight errors in plotting; for example, the radius through v should have intersected the divided circle at 19° 6′ from m, whereas, as plotted, it fell just short of 19°, an error perhaps of 8′. The sym-

bol of the scalenohedron, as indicated by the method, is $\frac{1}{2}a : a : -\frac{1}{3}a : c$, or $21\bar{3}1$. The radius through ς, and the chord at right angles to it from a_2, establish the relation on the horizontal axes, $\frac{3}{4}a : a - \frac{3}{7}a$, and also the length of the base-line Oz. The slope of the face, measured with the stereographic scale, was 80° 35′, calculated 80° 32′, and this angle plotted from the center intersected the vertical form z' at a distance $2{\cdot}993c$, practically $3c$. The symbol of the scalenohedron is therefore $\frac{3}{4}a : a : -\frac{3}{7}a : 3c$, or $43\bar{7}1$. The rhombohedron M was determined by the measurement $r \wedge M = 31°\ 10'$, giving $0001 \wedge M = 75°\ 47'$. This angle, plotted from the center, would intersect at $4c$, measured from x', or, instead of extending the drawing to such an extent, the slope may be plotted from c, as indicated in figure 21, and its intersection with the base-line, equal $\frac{1}{4}x'O$, determined. The symbol of M is therefore $40\bar{4}1$.

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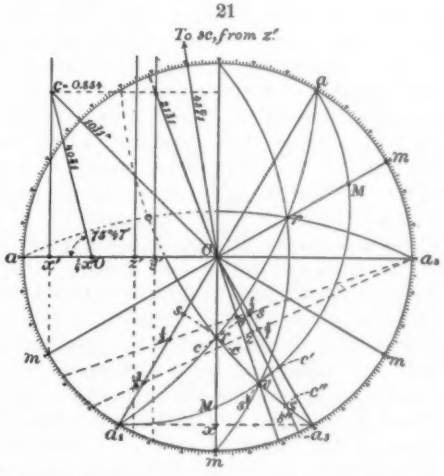

It seems worth while to call attention to a procedure employed in solving a complex problem encountered in the study of calcite crystals from Union Springs, N. Y.* The form to be considered is that of a scalenohedron v_1, in the same zone as v and ς, figure 21, but just a trifle steeper than v. The angle v on v_1 measured 3° 55′; hence since $a \wedge v = 23°\ 31'$, $a \wedge v_1 = 19°\ 36'$. Employing the same method of plotting as indicated in figure 21, the radius through the pole of v_1 was found to intersect the divided circle at 21° from m (theory 21° 3′), and a chord drawn from a_2, at right angles to it, gave

* This Journal (4) x, p. 237, 1900.

the following intersections with the horizontal axes, as determined by scale No. 4 of the printed sheets, $0{\cdot}573a : a : -0{\cdot}365a$. The foregoing figures, which indicate a parameter relation, are not easily interpreted, but their reciprocal values ($1{\cdot}746 : 1 : -2{\cdot}740$), which are equivalent to the indices, make it clear what the relation is, namely, $1\frac{3}{4} : 1 : -2\frac{3}{4}$. The distance 0001 to v_1, measured with the stereographic scale, was found to be 72° 35′ (theory 72° 30′), and the intercept on the vertical axis, plotted in the same manner as, for example, v in figure 21, was found to be almost exactly $\frac{4}{3}c$, the reciprocal (index) being $\frac{3}{4}$. The indices expressed as fractions are therefore $1\frac{3}{4}{\cdot}1{\cdot}-2\frac{3}{4}{\cdot}\frac{3}{4}$, or, cleared of fractions, $7{\cdot}4{\cdot}\bar{1}\bar{1}{\cdot}3$.

Orthorhombic System.

The example chosen for illustrating this system is a crystal of anglesite from Eureka, Utah, selected from a suite of beautiful specimens sent to the present writer by Mr. Maynard Bixby of Salt Lake City. In figure 22 the crystal is shown both in orthographic and clinographic projection, the figure having been drawn by Mr. W. E. Ford of the Sheffield Laboratory. The method employed in plotting is indicated by figure 23. The positions of the poles of the prism m, 110, and brachydome o, 011, were first located from the fundamental measurements, $m \wedge m$, $110 \wedge 1\bar{1}0 = 76°\ 16'$ and $o \wedge o$, $011 \wedge 0\bar{1}1 = 104°\ 24'$. These measurements are especially favorable for determining the lengths of the a and c axes, which are the tangents, respectively, of τ and π, figures 6 and 8, or the tangents of one-half the given angles; hence it is only necessary to draw two chords from b, intersecting the graduated circle at 76° 16′ and 104° 24′, measured from $0\bar{1}0$, figure 23. Thus the lengths of a and c, measured on the respective radii by scale No. 4, were found to be 0·786 and 1·289, calculated 0·786 and 1·289. The slope of the brachydome, $c \wedge o = 52°\ 12'$ ($\frac{1}{2}$ of $o \wedge o$), may also be plotted in the upper left-hand quadrant, and the length of the c axis measured on a perpendicular erected at $0\bar{1}0$, as indicated. The macrodomes d and l will be considered next. These were located on the vertical diameter by means of the angles $c \wedge d = 39°\ 23'$ and $c \wedge l = 22°\ 19'$, and lines plotted at these angles in the upper left-hand quadrant intersect the perpendicular from a' ($c\,a'$ equals the length of the a axis) at distances equal respectively to $\frac{1}{2}$ and $\frac{1}{4}$ the length of the c axis, thus determining the symbols $d = 102$ and $l = 104$. The position of the pyramid p is determined by the intersections of the zones $a : o$ and $c : m$. Thus plotted, the slope of p, measured with the stereographic scale, was found to be 64° 30′, calculated 64° 24′, and a line drawn at this angle from the center meets

the perpendicular from x′ at a distance equal to the length of the *c* axis; hence the symbol of *p* is 111. The pyramid *y*, in the zone *o* : *p*, was determined by the angle $o \wedge y = 26° 42'$, from which $a \wedge y = 63° 18'$; hence a small circle *sc*, drawn at 63° 18′ from *a*, figure 23, fixes the position of *y*. A radius through *y* was found to intersect the divided circle at 57° 30′ from *a*, 100, which corresponds with the pole of the prism *n*, and a chord from *b*, at right angles to this line, intersects the front radius at a distance equal to 2*a*. The intercepts on the first and second axes of *n*, *y*, and a third face in the zone, *μ*, are therefore 2*a* : *b*, the indices of *n* being 120. The slope

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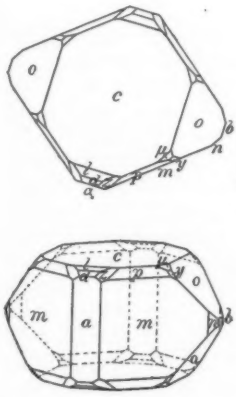

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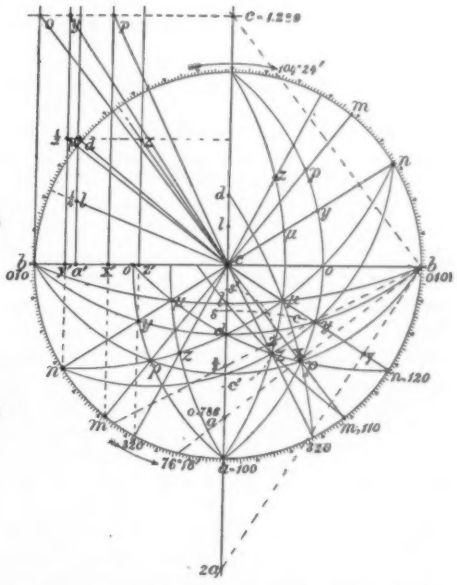


of *y*, measured with the stereographic scale, was found to be 56° 45′, calculated 56° 48′, and a line at this angle intersects the perpendicular from y′ at a distance equal to the length of the *c* axis; hence the parameter relation of *y* is 2*a* : *b* : *c*, the indices being 122. The pyramid *μ* was located by the measurement $c \wedge \mu = 37° 23'$, and a line at this angle meets the perpendicular from y′ at a distance equal to $\frac{1}{2}c$; hence the parameter relation of *μ* is 2*a* : *b* : $\frac{1}{2}c$, the indices being 124. The pyramid *z*, in the zone *d* : *p*, was located by the measurement $d \wedge z = 24° 49'$. This was done by first determining the zone *n*, *p*, *d*, *μ* and *o* by means of the great circle protractor,

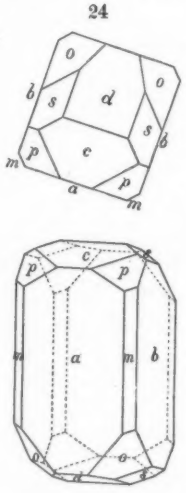
and then constructing a small circle s' c' about d at a distance of 24° 49′. A chord from b at right angles to the radius through z was found to intersect the front radius at $\frac{2}{3}a$. The slope of z, measured with the stereographic scale, was 54° 15′, calculated 54° 16′, and a line at this angle intersects the perpendicular from z' at a distance equal to $\frac{1}{2}c$. The parameter relation of z is therefore $\frac{2}{3}a : b : \frac{1}{2}c$, giving as the indices 324. In addition to the lines needed for the graphical solution of the foregoing problem, numerous zones are shown in figure 23 which were easily determined by means of the great circle protractor. The figure indicates that, starting with the poles of m (110) and o (011), it would have been a simple matter to have determined the location of the poles and the symbols of all the forms by no other means than zonal relations.

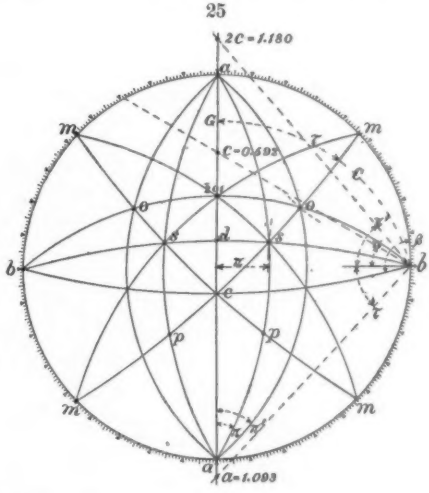
Monoclinic System.

The graphical methods employed in this system may be illustrated by pyroxene, a crystal of which is represented in orthographic and clinographic projection in figure 24. The figure, which represents a common habit of pyroxene from northern New York and Canada, was drawn by Mr. H. H. Robinson. As fundamental measurements the following were chosen: $m \wedge m$, $110 \wedge 1\bar{1}0 = 92° 50'$; $a \wedge c = 100 \wedge 001 = 74° 15'$; and $d \wedge s$, $\bar{1}01 \wedge \bar{1}11 = 29° 35'$. In stereographic projection, figure 25, the location of the poles of the prism m and of the base c, the latter by means of the stereographic scale, need no special comment. The construction of the great circles through m and c is then an easy matter, and the angles which they make at c with the vertical diameter are equivalent to τ of figures 6 and 8. The measurement of τ, 47° 30′, was made on the great circle GC at 90° from c.* Since γ, figure 6, is 90° in the monoclinic system, the tangent of τ must equal the length of the a axis; hence τ was laid off from b, and a determined as 1·093, calculated 1·092. Since $d \wedge s = 29° 35'$, $b \wedge s$ must be the complementary angle, 60° 25′; hence the pole of s was located by the intersection of a small circle (60° 25′ from b) with the great circle through c and m. Great circles through a and s and b and s were then drawn, thus determining the poles of p and d. The angle π, compare figures 6 and 8, was measured on the great circle (diameter) at 90° from a, and found to be 30° 35′; hence, referring to figure 6, since α is 90°, the tangent of π must equal the length of the c axis, which, when plotted from b, was found to be 0·592, calculated 0·589. The arcs mp and mc, measured with the small circle

* This Journal (4), xi, p. 18, 1901.

protractor, were found to be 45° 10′ and 79° 20′, calculated 45° 20′ and 79° 10′. By means of the stereographic scale $c \wedge d$ was determined as 31° 10′, calculated 31° 20′. The poles of the pyramid *o* were located by means of the measurement $m \wedge o = 35° 30'$, a small circle from *m*, $\bar{1}10$, being used. The great circle *ao* made an angle, π', of 49° 45′ at *a*, which, when plotted from *b*, was found to intersect the vertical radius at





1·180, practically 2*c*, the calculated value being 1·178; hence the axial relation of *o* is $-a : b : 2c$, the indices being $\bar{2}21$. The poles of *o* could also have been located by constructing a great circle through *m* and *s*, 110 and $\bar{1}11$, thus determining $\bar{2}01$, and then a second great circle through *b* and $\bar{2}01$.

For the purpose of showing the adaptability of the stereographic projection to measurements made with the two-circle goniometer, and also for illustrating another method of treating the monoclinic system, a problem encountered in the study of azurite crystals from Broken Hills, New South Wales, will be presented. The crystals, which are exceptionally beautiful, were measured and figured by Mr. Ralph G. VanName. They are lengthened in the direction of the ortho axis, like the ordinary development of epidote, and the habit is well illustrated by figure 26, drawn in clinographic projection with the *b* axis to the front. The crystal was orientated on the goniometer with the orthodome zone horizontal and the pinacoid *a*, 100, vertical, thus making an imaginary clino-pinacoid the polar face, although the form was not present on the crystal.

In the stereographic projection, figure 27, the angles φ, determined by the readings of the vertical circle, were laid off on the divided circle, starting from a, 100, and the angles ρ, given by the readings of the horizontal circle, were plotted on their respective diameters by means of the stereographic scale. The angles for making the projection shown in figure 27 are as follows:

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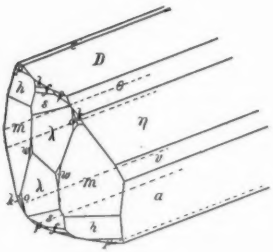

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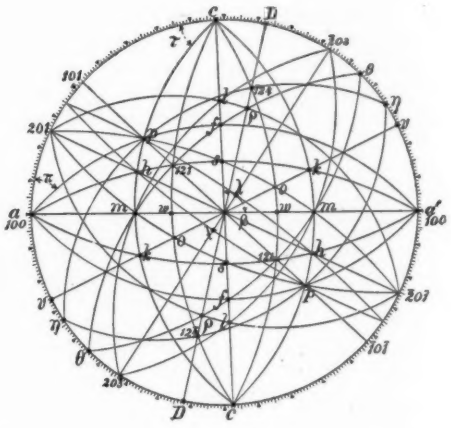

	φ	ρ		φ	ρ
a, 100,	00° 00′	90° 00′	D, $\bar{1}04$,	102° 15′	90° 00′
m, 110,	"	49 39	ϱ, $\bar{1}34$,	"	57 10
w, 120,	"	30 29	λ, $\bar{2}{\cdot}18{\cdot}3$,	122 59	12 43
h, 221,	25 18	53 02	θ, $\bar{1}01$,	134 51	90 00
p, 111,	42 50	59 06	η, $\bar{3}02$,	146 32	"
c, 001,	87 36	90 00	v, $\bar{2}01$,	153 47	"
l, 023,	"	59 37	k, $\bar{2}21$,	"	52 08
f, 011,	"	48 40	o, $\bar{2}41$,	"	32 44
s, 021,	"	29 36			

Having located the poles of the several faces, the zones shown in figure 27 were easily found by means of the great circle protractor. Starting, then, with the assumption that the symbols of two poles are known, for example, m, 110, and p, 111, it is possible to determine the symbols of the remaining forms by no other means than that afforded by zonal relations. As it is the object of this paper, however, to indicate the methods of graphical solution, the problem may be dealt with in a manner analogous to that employed in the orthorhombic system, since the b axis is at right angles to the plane of the a

and c axes. In order not to complicate figure 27 to too great an extent, the solutions depending upon plane trigonometry were worked out on a second divided circle, shown in figure 28. Having located the poles a, 100, and c, 001, the vertical and clino axes are represented by diameters at 90° from them, as indicated by broken-dashed lines; the lower half of the vertical diameter, however, may be employed for plotting the relations of the b axis, the length of which is unity. Referring to figure 27, the angles π and τ (compare figures 6 and 8) were measured, respectively, by the stereographic scale as 41° 20′ and 40° 20′, and these inclinations plotted from a and c, figure 28, determine the lengths of the c and a axes, which were

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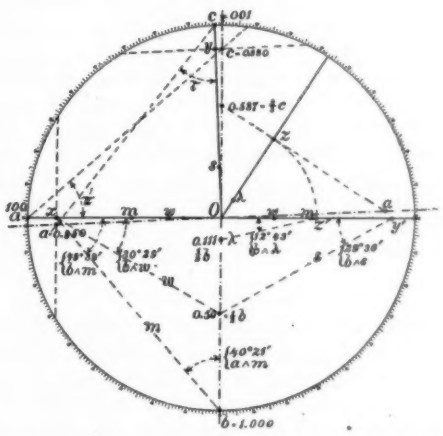

found to be as follows: $c=0{\cdot}880$ and $a=0{\cdot}850$, calculated, $c=0{\cdot}880$ and $a=0{\cdot}850$. In order to determine the relations of the prisms m and w, through unity on the a axis, a line was drawn at right angles to the radius through m and w, thus fixing a base-line Ox; then from x the inclinations of m and w (the ρ angles), 49° 39′ and 30° 29′, are plotted, and, as shown in figure 28, they intercept the lower radius at unity and one-half, respectively. Since the lower radius is taken to represent the b axis, the axial relation of m is $a : b : \infty c$, and of w, $a : \frac{1}{2}b : \infty c$, the indices being 110 and 120. Naturally the reverse of this method may be employed to advantage for determining the length of the a axis in this system, when the inclination β and the prismatic angle are given. For determining the symbol of a clinodome, for example s; through unity on the c axis draw a line at right angles to the radius through s,

thus determining the base-line Oy, and from y' (the distance Oy transferred to the horizontal diameter) lay off the ρ angle of s, 29° 36′, which intercepts the lower radius (b axis) at one-half; hence the axial ratio of s is $\infty a : \frac{1}{2}b : c$, the indices being 021. For a pyramidal face, for example λ, through unity on the a axis, a line at right angles to the radius through λ was drawn, which in figure 28 was found to intercept the vertical axis at 0·587, or exactly $\frac{2}{3}c$. Thus the intercept on the vertical axis and the base-line Oz are determined. From z', on the horizontal diameter, a second line was drawn at an inclination of 12° 43′, the ρ value of λ, which intersects the lower radius at 0·111, or $\frac{1}{9}b$. The axial ratio of λ is therefore $-a : \frac{1}{9}b : \frac{2}{3}c$, the indices being $\bar{2}\cdot 18\cdot 3$. Thus it makes no difference how complex the symbol may be, it is only necessary to keep in mind a few simple principles and the result is quickly obtained.

Finally, having made a projection such as shown in figure 27, the small circle protractor may be applied to it and the distances between any desired poles determined. Some results actually obtained in this way are as follows:

	Meas.	Cal.		Meas.	Cal.		Meas.	Cal.
$c \wedge m$,	88° 10′	88° 10′	$c \wedge k$,	71° 25′	71° 25′	$a \wedge p$,	50° 50′	51° 00′
$c \wedge p$,	52 30	52 28	$c \wedge o$,	77 24	77 25	$a' \wedge k$,	45 05	44 55
$c \wedge h$,	68 10	68 12	$m \wedge p$,	35 45	35 42	$a' \wedge o$,	61 05	60 59

Triclinic System.

For illustrating the application of graphical methods to this system a somewhat complex crystal of anorthite has been chosen, shown in orthographic and clinographic projection in figure 29. The crystal was studied and figured by Mr. J. C. Blake. The following were selected as fundamental measurements for making the stereographic projection, figure 30, and solving the problem:

$b \wedge m$, $010 \wedge 110 = 58° 04′$	$m \wedge e$, $110 \wedge 001 = 65° 53′$
$m \wedge M$, $110 \wedge 1\bar{1}0 = 59\ 29$	$b \wedge e$, $010 \wedge 021 = 43\ 12$
$b \wedge c$, $010 \wedge 001 = 85\ 50$	

Having located b, m and M on the divided circle, the position of 100 was first determined by the relation of four faces in a zone, explained on page 260, b, m and M being, respectively, the first, second and fourth faces, and 100 the unknown third face. This problem, as solved by itself on a separate sheet, is shown in figure 31. The lines of reference Ox and Oy are at right angles respectively to bb' and MM'. A line drawn from x, at right angles to the radius through m, intersects Oy at a point marked $\frac{1}{2}$. By solving the equation given on page 262 the ratio of the cotangents is found to be $\frac{1}{2} : 1$, hence a line from x to the point 1 on the line Oy determines the direction of the pinacoid 100. A line from the center at

right angles to xy fixes the pole of 100, which was found to be 87° 5′ from b, calculated 87° 6′. Having located the pole 100, the direction Oy', parallel to xy, may now be taken as the second line of reference. Lines from x to $\frac{1}{3}Oy'$, both to the right and left of the center, intercept the divided circle at 58° 50′ and 62° from $-x$, and angles equal to one-half of these values

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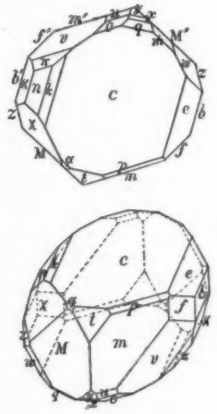

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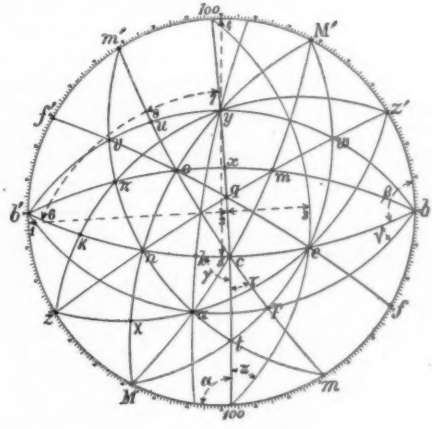

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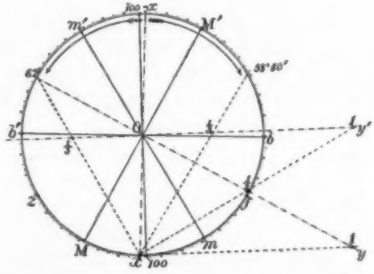

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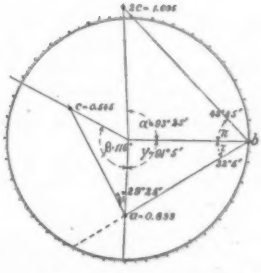


(page 260) give the inclinations $b \wedge f$ and $b' \wedge z$, namely, 29° 25′ and 31°, calculated 29° 29′ and 30° 58′. The indices of f and z are therefore 130 and 1$\bar{3}$0. The pole c, figure 30, was next located from the measurements $b \wedge c$ and $m \wedge c$, small circles about the poles b and m serving for this purpose. The small circles are not shown in the figure, but that about b, having a long radius, was constructed by means of the curved ruler,* that about m by means of a radius taken from scale No. 2 of the sheets. Having located c, the great circles b,c,b' ; m,c,m'; and 100,c, $\bar{1}00$ were drawn, thus determining the angles α, β,

* The Stereographic Projection and its Possibilities, loc. cit., p. 12.

γ and τ; compare figures 6 and 8. The angle a was measured by means of the stereographic scale on the diameter 1 to 2, figure 30, and found to be 93° 25′, calculated 93° 14′. Similarly β was measured on the diameter 4 to 5, and found to be 116°, calculated 115° 56′. To measure γ and τ, a great circle at 90° from c was first constructed.* The supplement of γ, from 6 to 7, was then determined as 88° 55′ by means of the small circle protractor, giving as the value of γ, 91° 5′, calculated 91° 12′. In like manner the arc from 7 to 8 was measured, giving 32° 5′ as the value of τ. On still a third sheet, shown in figure 32, the angles a, β and γ were plotted, and also τ, the latter determining the length of the brachy axis, a=0·636, calculated 0·635. It is still necessary to make use of the fifth fundamental measurement, from b to e, in order to determine the length of the vertical axis. By means of a small circle about b, figure 30, the position of e, on the great circle b,c, was located, and a great circle through 100, e and $\bar{1}00$ determines π. The value of π, measured on the diameter from 2 to 3, was found to be 45° 45′, and when plotted as shown in figure 32, the length of $2c$ was found to be 1·095; hence c=0·5475, calculated 0·550. The value obtained directly from π in this case is $2c$, because the symbol of e is 021.

Having located, as in figure 30, the poles b, m, 100, M, c and e, and also f and z from figure 31, the remaining forms of the crystal were easily identified by means of zonal relations and the measurement of a few angles. The construction of the zones shown in figure 30 would have proved a laborious task had it not been for the great circle protractor. This was used not only for determining the zones, but, far more important, its graduation furnished the means of getting the radii of the circular arcs from scale No. 1 of the sheets.

		Meas.	Cal.	Error.
$c \wedge t$,	001 $\wedge$ 201,	41° 30′	41° 28′	+ 2
$c \wedge q$,	001 $\wedge$	34 45	34 46	− 1
$c \wedge x$,	001 $\wedge$ $\bar{1}01$,	51 40	51 26	+14
$c \wedge y$,	001 $\wedge$ $\bar{2}01$,	81 30	81 14	+16
$c \wedge p$,	001 $\wedge$ 111,	33 10	33 17	− 7
$c \wedge \alpha$,	001 $\wedge$ 1$\bar{1}$1,	34 35	34 10	+25
$c \wedge m$,	001 $\wedge$ $\bar{1}$11,	54 10	54 17	− 7
$c \wedge o$,	001 $\wedge$ $\bar{1}\bar{1}$1,	58 00	57 52	+ 8
$c \wedge u$,	001 $\wedge$ $\bar{2}\bar{2}$1,	85 00	84 50	+10
$c \wedge \kappa$,	001 $\wedge$ 0$\bar{6}$1,	75 20	75 10	+10
$c \wedge n$,	001 $\wedge$ 0$\bar{2}$1,	47 00	46 46	+14
$c \wedge k$,	001 $\wedge$	18 55	18 38	+17
$b' \wedge \chi$,	0$\bar{1}$0 $\wedge$	52 20	52 11	+ 9
$b' \wedge \pi$,	0$\bar{1}$0 $\wedge$	34 10	34 20	−10
$b' \wedge v$,	0$\bar{1}$0 $\wedge$	38 05	38 16	−11
$b' \wedge w$,	010 $\wedge$	38 55	38 42	+13

* The Stereographic Projection and its Possibilities, loc. cit., p. 18.

A list of measurements made with the small circle protractor is given in the table on the foregoing page. The average of the errors is 11′, with errors of more than a quarter of a degree in only three instances. In figure 30, the angle between the great circles *b*,*c* and *b*,*p* determines ν (compare figures 6 and 8), which was found to measure 29° 25′. The angle ν, plotted from unity on the *a* axis, as shown in figure 32, gives another method for determining the length of the *c* axis; in this case *c* was measured as 0·545, calculated 0·550.

Conclusion.

In the foregoing pages the attempt has been made to indicate not only the methods of plotting problems in the several systems, but, also, to give an idea of the accuracy of the results thus obtained. In judging the accuracy of the results it must be kept in mind that the scale employed was quite small, the engraved circle being only 14^{cm} ($5\frac{1}{2}$ in.) diameter. Each problem presented was worked out from fundamental measurements, as would have been the case if done by numerical calculation, and the results indicate that for all practical purposes graphical methods are in every way satisfactory. The lengths of axes have frequently been obtained correctly to the third place of decimals, and never varied more than one in the second place, and measurements of arcs and angles by the stereographic protractors have been reasonably close to the calculated values in all cases. After becoming familiar with the principles involved in dealing with the projection—and they are not difficult to understand—any problem may be worked out without the use of prescribed formulas, or tables of any kind, and this the writer believes is one of the great advantages of the method. Then, too, it is a very simple step to proceed from a graphical to a numerical solution, for the principles involved are identical, and it is only necessary to apply the formulas of spherical and plane trigonometry in order to obtain the desired results by calculation. The writer has never made use of formulas for solving even the most complex problems of crystallography, other than those needed for the general cases which arise in dealing with spherical and plane triangles, and it is his belief that the too general use of prescribed formulas is, if anything, a hindrance to true progress in crystallography. Graphical methods will also be found to have very decided value as giving a ready means of checking the results of numerical calculations. During the past two years, since they have been in use, numerous cases have arisen where mistakes in calculation have been made, at times amounting to less than a degree, but they have been almost

instantly detected by applying the protractors to the stereographic projections. Generally it has been found that mistakes were due to errors (carelessness, perhaps, is a better term) in such simple processes as addition and subtraction.

In an earlier communication* a description was given of blackboard appliances which have proved most useful for demonstrations of the stereographic projection on a rather large scale before a class. Thus, in the discussion of any problem which may arise, a projection may be made in a few minutes, from which the zonal relations, symbols and angles of the forms may be determined. As a demonstration of the practicability of the method, a projection of pyroxene, like figure 25, page 277, was constructed from fundamental measurements, and the following determinations made, the time consumed being nineteen minutes:

Given, $m \wedge m''' = 92° 50'$; $c \wedge p = 33° 49'$ and $a \wedge c = 74° 10'$.

Axes determined, $a : b : c = 1{\cdot}11 : 1 : 0{\cdot}585$.

Axes calculated, $a : b : c = 1{\cdot}092 : 1 : 0{\cdot}589$.

Angles.	Meas.	Cal.	Angles.	Meas.	Cal.
$m \wedge c$, $110 \wedge 001$	$79°$	$79° 9'$	$o \wedge o$, $\bar{2}21 \wedge \bar{2}\bar{2}1$	$84'$	$84° 11'$
$c \wedge d$, $001 \wedge \bar{1}01$	31	$31\ 20$	$c \wedge o$, $001 \wedge \bar{2}21$	65	$65\ 21$
$p \wedge p$, $111 \wedge 1\bar{1}1$	$48\frac{1}{4}$	$48\ 29$	$a \wedge p$, $100 \wedge 111$	$53\frac{1}{2}$	$53\ 38$
$s \wedge s$, $\bar{1}11 \wedge \bar{1}\bar{1}1$	$59\frac{1}{4}$	$59\ 11$	$a \wedge s$, $\bar{1}00 \wedge \bar{1}11$	$76\frac{1}{4}$	$76\ 34$
$c \wedge s$, $001 \wedge \bar{1}11$	$42\frac{1}{2}$	$42\ 2$	$a \wedge o$, $\bar{1}00 \wedge \bar{2}21$	$62\frac{1}{2}$	$61\ 32$

It should be stated that the foregoing problem was executed with blackboard crayon, and with beam-compass and scales graduated to every fifth degree only.

Finally the writer would state that in his own laboratory the graphical methods have proved most serviceable, and it is believed that by means of them a far better insight into mathematical crystallography and the meaning of zonal relations and angles has been gained by the students, than when other methods were employed. There is no wish to discourage numerical calculations; such must be made, and facility in making them must be acquired, but the graphical methods, if properly interpreted, are, if anything, a decided help, for they give meaning to the calculations, which, far too often, are made by prescribed formulas, wholly meaningless to the average student.

* The Stereographic Projection and its Possibilities, loc. cit., p. 140.

Sheffield Laboratory of Mineralogy and Petrography,
Yale University, New Haven, May 1902.

ART. XXXI.—*The Estimation of Bromic Acid by the Direct Action of Arsenious Acid;* by F. A. GOOCH and J. C. BLAKE.

[Contributions from the Kent Chemical Laboratory of Yale University—CXI.]

IN a former paper from this laboratory* it has been shown that iodic acid may be reduced quantitatively by arsenious acid. In the work of which the present paper is an account the attempt has been made to apply arsenious acid similarly to the quantitive estimation of bromic acid, according to the equation

$$3H_3AsO_3 + HBrO_3 = 3H_3AsO_4 + HBr.$$

In the following series of experiments, made to discover the limits within which regularity of action might be expected, definite amounts of arsenious oxide dissolved in acid potassium carbonate were mixed with measured portions of a solution of potassium bromate, sulphuric acid was introduced in the amounts indicated, and, after standing either at the ordinary temperature, on the steam-bath or at the boiling temperature, potassium acid carbonate was added and the arseniate remaining was titrated with iodine to color, the indication being confirmed by addition of starch. The conditions of acidity, the excess of arsenious oxide, the dilution, the time of action, and the temperature were varied within wide limits. The potassium bromate for this particular series of experiments was thrice recrystallized from water, dried at 110°, and made up in solution containing 2·8 grms. to the liter. Of this solution 25 or 50$^{cm^3}$ were measured out for each experiment.

TABLE I.

Volume not exceeding 200$^{cm^3}$.

$KBrO_3$ taken. grm.	As_2O_3 taken. grm.	H_2SO_4 (1 : 1) taken. cm^3.	Time of digestion.	As_2O_3 unchanged. grm.	As_2O_3 oxidized. grm.	Error in terms of $KBrO_3$. grm.
Heated at the boiling temperature.						
0·1400	0·4950	10	30 min.	0·2476	0·2474	0·0008—
0·1400	0·4950	10	30 "	0·2480	0·2470	0·0010—
0·1400	0·6188	10	20 "	0·3708	0·2480	0·0006—
0·1400	0·7425	8	25 "	0·4941	0·2484	0·0003—
0·1400	0·7425	8	25 "	0·4943	0·2482	0·0004—
0·1400	0·6188	7	20 "	0·3704	0·2484	0·0003—
0·1400	0·6203	7	20 "	0·3720	0·2483	0·0004—

* Gooch and Pulman, this Journal, xii, p. 450 (1901).

TABLE I—*Continued.*

Volume not exceeding 200^{cm3}.

$KBrO_3$ taken. grm.	As_2O_3 taken. grm.	H_2SO_4 (1 : 1) taken cm_3.	Time of digestion.	As_2O_3 unchanged. grm.	As_2O_3 oxidized. grm.	Error in terms of $KBrO_3$. grm.
			Heated at the boiling temperature.			
0·1400	0·6188	5	15 min.	0·3712	0·2476	0·0008 —
0·1400	0·4950	3·5	15 "	0·2480	0·2470	0·0010—
0·1400	0·4950	3·5	15 "	0·2482	0·2468	0·0011 —
[0·1400	0·4950	2·5	15 "	0·2629	0·2321	0·0097 —]
0·0700	0·2475	5	15 "	0·1240	0·1235	0·0005 —
0·0700	0·2475	5	15 "	0·1239	0·1236	0·0004 —
0·0700	0·2475	5	15 "	0·1258	0·1217	0·0015 —
0·0700	0·2475	5	15 "	0·1244	0·1231	0·0007 —
0·0700	0·2475	5	10 "	0·1239	0·1236	0·0004 —
0·0700	0·2475	5	10 "	0·1237	0·1238	0·0003 —
0·0700	0·1584	5	10 "	0·0345	0·1239	0·0003 —
0·0700	0·1584	5	10 "	0·0357	0·1227	0·0009 —
0·0700	0·1584	5	10 "	0·0356	0·1228	0·0009 —
0·0700	0·1584	5	10 "	0·0353	0·1231	0·0007 —
0·0700	0·1881	5	10 "	0·0649	0·1232	0·0007 —
0·0700	0·1881	5	10 "	0·0640	0·1241	0·0002 —
0·0700	0·1881	5	10 "	0·0649	0·1232	0·0007 —
0·0700	0·1881	5	5 "	0·0652	0·1229	0·0008 —
0·0700	0·1881	5	5 "	0·0652	0·1219	0·0008 —
0·0700	0·2475	2·5	10 "	0·1238	0·1237	0·0004 —
0·0700	0·2475	2	10 "	0·1235	0·1240	0·0002 —
0·0700	0·2475	1·15	10 "	0·1242	0·1233	0·0006 —
0·0700	0·2475	1·15	10 "	0·1240	0·1235	0·0005 —
[0·0700	0·2475	1·15	5 "	0·1300	0·1175	0·0038 —]
			Heated on the steam-bath —80°.			
0·1400	0·4950	10	150 min.	0·2476	0·2474	0·0008 —
0·1400	0·4950	10	150 "	0·2476	0·2474	0·0008 —
0·1400	0·4950	4	240 "	0·2473	0·2477	0·0007 —
0·1400	0·4950	4	240 "	0·2475	0·2475	0·0008 —
0·1400	0·4950	4	180 "	0·2472	0·2478	0·0006 —
0·1400	0·4950	4	180 "	0·2470	0·2480	0·0005 —
0·1400	0·4950	3·5	90 "	0·2475	0·2475	0·0008 —
0·1400	0·4950	3·5	90 "	0·2476	0·2474	0·0008—
[0·0700	0·2475	1·15	30 "	0·1622	0·0853	0·0217—]
			Digested at the ordinary temperature.			
0·1400	0·4950	4·	46 hrs.	0·2480	0·2470	0·0005 —
0·1400	0·4950	3·5	41 "	0·2475	0·2475	0·0008 —
0·1400	0·4950	3·5	41 "	0·2470	0·2480	0·0005 —
0·1400	0·4950	3·5	17 "	0·2490	0·2460	0·0016—
0·1400	0·4950	3·5	17 "	0·2492	0·2458	0·0017—

An examination of these results discloses the fact that for conditions varying within a rather wide range the oxidation of the arsenious oxide reaches a fairly definite limit. The bromate effects practically the same proportionate oxidation of arsenious oxide in a volume of 200$^{cm^3}$ or less, whether the sulphuric acid of half-strength present amounts to 3·5$^{cm^3}$ or 10$^{cm^3}$, and whether the time of digestion is 15 minutes or 30 minutes at the boiling temperature, one and one-half or four hours on the steam-bath, or two days at the ordinary temperature. Setting aside those experiments in which the addition of acid did not exceed the equivalent of alkali carbonate present by more than 1$^{cm^3}$, the average absolute variation from theory of the entire list of forty-two experiments amounts to 0·0007—grm. in terms of bromate, individual variations departing from the average by about the same figure. The obvious meaning of this fact seems to be that the slight error is due to impurity in the potassium bromate employed and not to incomplete oxidizing action on the part of the bromate.

In the following series of experiments another preparation of bromate was employed, and its value was fixed by reduction with acidified potassium iodide and titration of the iodine set free according to the method formerly proposed by Kratchmer.* The rate at which the action proceeds, according to the equation

$$6HI + HBrO_3 = HBr + 3H_2O + I_6,$$

has been investigated by Ostwald,† by Noyes,‡ and by Judson and Walker.§ Time of action, proportion of iodide to bromate, excess of acid, and dilution are all, within limits, determining factors in the reaction; but in the analytical process it is usually assumed that the reaction goes soon to completion if free acid and a moderate excess of potassium iodide are present. In the following table are recorded the results of experiments in which measured amounts of standard solutions of potassium bromate (approximately 2·8 grms. to the liter) were treated with potassium iodide and hydrochloric or sulphuric acid for definite times in glass-stoppered bottles, the iodine liberated being determined by titration with sodium thiosulphate standardized against nearly decinormal iodine of value fixed by comparison with decinormal arsenious oxide dissolved in acid potassium carbonate.

* Zeit. Anal. Chem., xxiv, 546 (1885).
† Zeit. Phys. Chem., ii, 127 (1888).
‡ Zeit. Phys. Chem., xix, 599 (1896).
§ Jour. Chem. Soc., lxxiii, 410 (1898).

TABLE II.

A

	$KBrO_3$ = Iodine taken. grm.	Iodine taken. grm.	KI taken. grm.	H_2SO_4 (1 : 1) cm^3.	Time of standing. hrs.	Approximate volume. cm^3.	Iodine found. grm.	Error in terms of $KBrO_3$ grm.
[(1)	0·1410	0·6423	1	5	none	150	0·6223	0·0044—
[(2)	0·1410	0·6423	1	5	none	200	0·5929	0·0108—]
(3)	0·1400	0·6378	3	5	½	100	0·6343	0·0008—
(4)	0·1400	0·6378	3	5	½	100	0·6329	0·0011—
(5)	0·1400	0·6378	3	5	½	100	0·6329	0·0011—
(6)	0·1408	0·6416	3	5	22	100	0·6396	0·0004—
(7)	0·1408	0·6416	3	5	22	100	0·6364	0·0011—
(8)	0·1408	0·6416	3	5	22	100	0·6381	0·0008—
(9)	0·1400	0·6378	3	2·5	½	100	0·6340	0·0008—
(10)	0·1400	0·6378	3	2·5	½	100	0·6336	0·0009—
(11)	0·1400	0·6378	3	2·5	½	100	0·6336	0·0009—
(12)	0·1400	0·6378	3	1	½	100	0·6343	0·0008—
(13)	0·1400	0·6378	3	0·5	½	100	0·6331	0·0010—

B

				HCl Sp. gr. 1·18 cm^3.				
(14)	0·1400	0·6378	3	8	½	100	0·6336	0·0009—
(15)	0·1400	0·6378	3	8	½	100	0·6329	0.0011—
(16)	0·1400	0·6378	3	8	½	100	0·6336	0·0009—
(17)	0·1400	0·6378	3	4	½	100	0·6336	0.0009—
(18)	0·1400	0·6378	3	4	½	100	0·6333	0·0010—
(19)	0·1400	0·6378	3	4	½	100	0·6340	0·0008—
(20)	0·1400	0·6378	3	4	1	100	0·6336	0·0009—
(21)	0·1400	0·6378	3	4	1	100	0·6333	0·0010—
(22)	0·1400	0·6378	3	4	1	100	0·6336	0·0009—

In experiments (1) and (2) the excess of potassium iodide was only about 20 per cent over the amount demanded by theory, the time of standing was only the few minutes required for the manipulation of the process, and the dilution was considerable. It is obvious that under these conditions the reaction is very incomplete. On the other hand, a glance at the table makes it evident that the oxidation in all other experiments, whether in A or B, proceeds to practically the same point, showing similar errors. So it appears that the variation in the amount of acid above the minimum, the kind of acid (whether sulphuric or hydrochloric), and the time above the minimum half-hour, within the limits defined, are without apparent effect upon the reaction in the presence of the amount of potassium iodide used, approximately four times

the amount required by theory. The balancing error due to the evolution of iodine by the action of atmospheric oxygen upon the acidified solution of the iodide was found by experiment to vary with the strength of the acid and the time of exposure, from 0·0001 grm. to 0·0003 grm. expressed in terms of the bromate, and these values are not greater than the differences observed between parallel determinations of the same sort. Probably, therefore, all the errors as shown in the table should really be increased a trifle to approximate the truth, notably those of the experiments allowed to stand the longest period, twenty-two hours.

The average apparent error of the process as applied to this particular sample of bromate is 0·0009– grm.; and 2·5$^{cm^3}$ of sulphuric acid of half-strength (1:1) or the equivalent amount of hydrochloric acid, 4$^{cm^3}$ of the acid of sp. gr. 1·18, in the presence of about 3 grms. of potassium iodide, complete the action within a half hour, at a dilution of 100$^{cm^3}$, as far as it will go under any of the conditions tried. The phenomenon noted by Ostwald,* that small amounts of hydrochloric acid tend to force the reaction more rapidly than equivalent amounts of sulphuric acid, does not appear in these experiments, no doubt because the action was pushed to the limit by the smallest amount of the weakest acid employed.

The error of deficiency shown again appears to be due to impurity in the sample of bromate rather than to incompletness of the reaction. If the reaction were incomplete it would be natural to look for the cause in the possibility of the inhibiting influence of the iodine set free,† but it was found in three parallel experiments that the introduction of ·5 grm. of free iodine dissolved in potassium iodide failed to influence the error appreciably. For the present purpose, however, the absolute purity of the bromate is not a matter of moment, if, as seems to be the case, Kratchmer's reaction indicates its value with accuracy, as the basis of experimentation. It seems safe to assume, then, that the average result of experiments (3) to (22) will give a very fair value for the sample of bromate investigated. That is to say, the experiments show an average deficiency in bromate amounting to 0·0009 grm., or to 0·64 per cent.

Portions of this bromate were taken for reduction by arsenious acid. Solutions not exceeding 200$^{cm^3}$ in volume, containing the bromate and a considerable excess of arsenious oxide acidified with sulphuric acid of half-strength, were boiled for periods varying from ten to forty-five minutes, neutralized with potassum acid carbonate, and titrated with iodine. The results are shown in Table III.

* Loc. cit., p. 131. † Judson and Walker, loc. cit., p. 411.

TABLE III.

	$KBrO_3$ taken. grm.	As_2O_3 taken. grm.	H_2SO_4 (1:1). cm^3.	Time in minutes.	As_2O_3 unchanged. grm.	As_2O_3 oxidized. grm.	Error in terms of $KBrO_3$. grm.
(1)	0·0701	0·1881	5	10	0·0661	0·1220	0·0014—
(2)	0·0701	0·1881	5	10	0·0650	0·1231	0·0009—
(3)	0·0701	0·2475	5	10	0·1232	0·1243	0·0002—
(4)	0.0701	0·2475	5	10	0·1236	0·1239	0·0004—
(5)	0·0701	0·2475	5	25	0·1234	0·1241	0·0003—
(6)	0·0701	0·2475	5	25	0·1234	0·1241	0.0003—
(7)	0·1402	0·4950	3	15	0·2479	0·2471	0·0012—
(8)	0·1402	0·4950	3	15	0·2476	0·2474	0·0010—
(9)	0·1400	0·6188	7	20	0·3708	0·2480	0·0004—
(10)	0·1400	0·6188	7	20	0·3710	0·2478	0·0005—
(11)	0·1400	0·6188	7	20	0·3706	0·2482	0·0003—
(12)	0·1400	0·6188	7	30	0·3708	0·2480	0·0004—
(13)	0·1400	0·6188	7	45	0·3711	0·2477	0·0006—

Here again, as in the experiments of Table I, the indications of the process of reduction of the bromate by arsenious acid, point to a slight deficiency in the oxidizing power of the bromate. The mean deficiency, 0·0006 grm., differs from the indications of the process of reduction of the same sample by the potassium-iodide method by about 0·0003+ grm.

The question now arises as to what is the impurity in the bromate. In a product recrystallized several times, and in one in which no chloride can be detected, as was the case with the bromate of these experiments, the impurity most natural to look for is potassium chlorate, which, might resist removal in the process of purification by recrystallization. The preparation of bromate upon which these last experiments were made was therefore tested by igniting it and treating the residue with potassium bichromate and sulphuric acid, volatilizing and collecting any chloro-chromic anhydride thus formed, and converting the last into lead chromate.* Traces of chlorine were thus found, which, not appearing in a similar test upon the unignited bromate, must have had their origin in chlorate intercrystallized with the bromate. In a former paper from this laboratory† it has been shown that a chlorate may be determined by adding to it in solution potassium iodide in known amount and an excess of an arseniate and sulphuric acid, boiling the mixture between definite limits of concentration, determining by titration with iodine the amount of arsenious oxide produced, and calculating the amount of chlorate present, from the difference between the amount of arsenious oxide thus produced and that which

* Gooch and Brooks, this Journal, xl, p. 287 (1890).
† Gooch and Smith, this Journal, xlii, p. 220 (1891).

should be produced if the whole amount of iodide added were allowed to act upon the arseniate alone. There appears to be no reason why a bromate treated by this process should not leave a similar record of its oxidizing power. A mixture of bromate and chlorate should, therefore, in this process, leave a record of the full amount of oxidation of which both together are capable. The following table contains the account of experiments made in this manner upon the sample of bromate the action of which in the iodide method and in the arsenious acid method is recorded in Tables II and III.

TABLE IV.

(H_2SO_4) (1:1) 20$^{cm^3}$; initial volume 105 to 170$^{cm^3}$; final volume 35$^{cm^3}$.

	$KBrO_3$ taken. grm.	H_2KAsO_4 taken. grm.	I value of KI taken. grm.	Iodine corresponding to As_2O_3 produced. grm.	Iodine corresponding to $KBrO_3$. grm.	Error in terms of $KBrO_3$. grm.
(1)	0·0700	2	0·4146	0·0948	0·3198	0·0002+
(2)	0·0700	2	0·4146	0·0954	0·3192	0·0000
(3)	0·0700	2	0·4146	0·0969	0·3177	0·0003—
(4)	0·0700	2	0·4146	0·0975	0·3171	0·0004—
(5)	0·1400	2	0·7832	0·1458	0·6374	0·0001—
(6)	0·1400	2	0·7832	0·1463	0·6369	0·0002—
(7)	0·1400	2	0·7832	0·1462	0·6370	0·0002—

The mean error of these determinations, in which all oxidizing material is calculated as bromate, is not far from 0·0001– grm.

In the case of still another preparation of potassium bromate, made by acting with commercial bromine on potassium hydroxide, crystallizing and recrystallizing several times, determinations by means of arsenious acid and by the arseniate-iodide process resulted as shown in the following statement:

TABLE V.

A.

Arsenious Acid Method.

(Volume not exceeding 100$^{cm^3}$.)

$KBrO_3$ taken. grm.	As_2O_3 taken. grm.	H_2SO_4 (1:1) grm.	Time in minutes.	As_2O_3 unchanged. grm.	As_2O_3 oxidized. grm.	Error in terms of $KBrO_3$ grm.
At the boiling temperature.						
0·0704	0·2475	5	10	0·1241	0·1234	0·0010—
0·0704	0·2475	5	15	0·1239	0·1236	0·0009—
0·0704	0·2475	5	15	0·1236	0·1239	0·0007—

TABLE V—*Continued.*

A.

Arsenious Acid Method.

(Volume not exceeding 100$^{cm^3}$.)

$KBrO_3$ taken. grm.	As_2O_3 taken. grm,	H_2SO_4 (1 : 1) grm.	Time in minutes.	As_2O_3 unchanged. grm.	As_2O_3 oxidized. grm.	Error in terms of $KBrO_3$ grm.
			On the steam bath,—80°.			
0·0704	0·2475	5	30	0·1241	0·1229	0·0013 −
0·0704	0·2475	5	30	0·1246	0·1234	0·0010 −
			At atmospheric temperature.			
0·0704	0·2475	5	10	0·2066	0·0409	0·0474 −
0·0704	0·2475	5	10	0·1991	0·0488	0·0426 −
0·0704	0·2475	5	30	0·1533	0·0922	0·0185 −
0·0704	0·2475	5	60	0·1231	0·1244	0·0004 −
0·0704	0·2475	5	120	0·1242	0·1233	0·0011 −
0·0704	0·2475	5	120	0·1238	0·1237	0·0009 −

B.

Arseniate-Iodide Method.

(H_2SO_4) (1 : 1) 20$^{cm^3}$; initial volume 110$^{cm^3}$; final volume 35$^{cm^3}$.

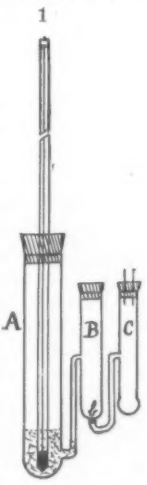
$KBrO_3$ taken. grm.	H_2KAsO_4 taken. grm.	I value of KI taken. grm.	Iodine corresponding to As_2O_3 produced. grm.	Iodine corresponding to $KBrO_3$. grm.	Error in terms of $KBrO_3$. grm.
0·0704	2	0·3812	0·0607	0·3205	0·0001 −
0·0704	2	0·3812	0·0588	0·3224	0·0003 +
0·0704	2	0·3812	0·0595	0·3217	0·0001 +
0·0704	2	0·3842	0·0590	0·3222	0·0002 +
0·0704	2	0·3812	0·0615	0·3197	0·0003 −
0·0647	2	0·3812	0·0839	0·2973	0·0004 +

The mean error of the arseniate-iodide process applied to this particular sample of bromate is 0·0001+ grm. in terms of bromate; the arsenious acid method shows a mean deficiency of about 0·0009 grm. for the smaller amount of bromate employed, if, as is obviously reasonable, those results are omitted from the averages which were obtained by standing at the ordinary temperature for periods less than one hour.

It appears, therefore, that the deficiency in the indications of the iodide process and the arsenious acid process are satisfactorily accounted for by the presence in the bromate of traces of chlorate; and that the oxidizing power of a bromate may be determined by boiling it in solution with a known excess of arsenious oxide and an excess of sulphuric acid, and determining the amount of arsenious oxide remaining unchanged. A chlorate, as we have found by direct experiment, is scarcely affected by this treatment.

ART. XXXII.—*Solubilities of Some Carbon Compounds and Densities of their Solutions;* by CLARENCE L. SPEYERS.

AT the present time we are more or less inclined to find in solution an action corresponding to vaporization, and as vaporization under ideal conditions is generally considered independent of the contents of the space into which the substance volatilizes, chemical action of course being excluded, so in forming dilute solutions we generally expect the act of solution to be independent of the medium into which the solute passes, that is, independent of the solvent. In some respects our expectations are justified and find their expressions in the van't Hoff laws; but on the other hand, we cannot fail to see that the solvent plays a very important part, for many substances refuse altogether to dissolve in certain solvents, and consequently the simplicity of the gaseous condition cannot be carried over directly to solutes without running the risk of straying away from the path leading to a satisfactory explanation of solution.



It was in the hope of finding that the different molecular aggregations of the solutes would explain their differences in solubility that the following experiments were made. It was in the hope of finding that in a saturated solution the osmotic pressure of the solute in the form of simple molecules would be the same in all solvents because the liquid phases are all balanced by the same solid phase, that is by the same undissolved solute. The large number of measurements of the solubilities of metallic salts were not available on account of ionic decomposition.

The same solutes and solvents were chosen which were used in determining heats of solution* and in determining molecular weights in concentrated solutions.†

The apparatus shown in figure 1 was used; the tube A was about 17^{cm} long and 2·5^{cm} wide; B was about 12^{cm} long and about 2·0^{cm} wide; C was about of the same size as B. Solution, excess of solute and thermometer were in A. At the bottom of B was a plug of filter paper, *b;* otherwise B was empty, and C was empty. After the tubes were charged, they were sunk in a water bath nearly to the tops of B and C. The solution and solute were kept stirred by air blown through C, the air escaping around the loosely fitting stopper of A. When

* Journ. Am. Chem. Soc., xviii, 146, 1896. † This Journal, xiii, 213, 1902.

the solvent was other than water, the air was dried by calcium chlorid.

About half an hour was needed to get the temperature of the water bath constant to 0·1° for ten minutes. When that was done, at the end of the ten minutes, the solution with undissolved solute was drawn over into B, and through the filter plug into C. When the solute was a nitrogenous body, the solution was analyzed by the Kjehldahl method; by specific gravity, when the solute was non-nitrogeneous. Evaporation to dryness and weighing the residue was altogether unsuitable, too much decomposition.

The solutions were believed to be in just the right condition, since the large mass of crystals present when the solution was drawn over must have prevented appreciable supersaturation on the one hand, and on the other, as the temperature was always falling at this time, though only very slightly, the solution must have been completely saturated.

The thermometer was carefully calibrated. It was divided into tenths and the temperature is probably correct to this quantity, but hardly correct to a smaller quantity on account of the uncertainty of the temperature of the exposed thread.

The examination and purification of solvents and solutes have already been described.*

The following tables give the results calculated to per cent gram-molecules, that is, to the number of gram-molecules of solute in 100 gram-molecules of solution at the accompanying temperature. The usual chemical formulæ were used in the calculations.

WATER.

Urea.		Urethane.		Chloral hydrate.		Succinimid.		Acetamid.		Resorcinol.	
0·0°	16·77	0·0°	3·61	0·0°	20·66	0·0°	1·58	0·0°	29·64	0·0°	9·78
11·0°	20·82	10·3°	6·09	11·3°	30·23	11·3°	2·74	10·6°	34·35	10·0°	13·27
19·8°	22·69	11·1°	6·62	23·7°	45·86	20·7°	4·23	19·9°	40·72	34·6°	23·67
31·7°	28·24	23·5°	43·70	38·1°	59·41	33·3°	9·91	32·9°	49·62	55·8°	36·74
51·4°	36·67	31·4°	68·91			69·3°	27·14	45·5°	60·14	79·8°	50·91
69·5°	43·15	37·0°	75·58					63·0°	77·10		

METHYL ALCOHOL.

Urea.		Urethane.		Acetanilid.		Naphthalene.		Acenaphthene.	
.0·0°	7·34	0·0°	31·18	0·0°	5·38	0·0°	0·87	0·0°	0·39
10·8°	8·71	10·6°	41·70	11·5°	7·02	14·6°	1·68	12·4°	0·38
21·7°	10·81	22·5°	58·58	22·8°	11·12	31·8°	2·97	30·7°	0·73
40·4°	15·96	40·9°	90·00	33·6°	13 96	48·0°	5·83	46·0°	1·55
61·2°	25·77			40·2°	17·05	59·9°	12·34	62·3°	2·46
				47·4°	23·72				
				60·9°	35·24				
				63·3°	33·33				

* This Journal, l. c.

ETHYL ALCOHOL.

Urea.		Urethane.		Acetanilid.		Naphthalene.		Resorcinol.		Acenaphthene.	
0·0°	1·95	0·0°	23·91	0·0°	5·01	0·0°	1·80	0·0°	34·37	0·0°	0·57
10·5°	3·04	10·5°	36·86	10·8°	6·84	8·6°	2·13	9·2°	37·69	10·0°	0·84
22·3°	4·07	21·7°	52·21	42·5°	17·93	31·8°	4·82	31·8°	41·84	30·3°	1·70
32·3°	5·61	30·9°	72·35	43·5°	15·40	46·9°	9·70	50·6°	47·07	49·8°	3·86
55·5°	9·18	40·5°	88·32	61·6°	31·36	69·8°	64·23	73·1°	58·03	71·6°	12·94
72·1°	14·40										

Phenanthrene.		Chloral hydrate.		Succininid.		Acetamid.		Benzamid.		p-Toluidin.	
0·0°	0·82	0·0°	34·35	0·0°	0·88	0·0°	18·53	0·0°	3·08	0·0°	20·72
10·9°	0·86	13·5°	41·08	11·1°	1·36	18·6°	32·87	10·4°	4·25	11·7°	33·88
32·1°	1·56	36·0°	83·16	24·2°	2·44	42·5°	56·06	32·6°	8·72	22·1°	50·90
47·0°	2·19	43·4°	92·32	43·7°	5·63	62·0°	78·92	50·4°	14·44		
70·2°	7·52			58·6°	11·49			72·2°	20·86		

PROPYL ALCOHOL.

Urethane.		Naphthalene.		Acenaphthene.	
0·0°	19·48	0·0°	2·09	0·0°	0·88
10·4°	32·27	10·4°	2·70	10·5°	0·97
21·6°	53·31	30·3°	5·34	31·1°	1·88
30·4°	68·75	50·3°	15·34	50·3°	4·37
40·7°	85·74	68·5°	62·9	73·4°	19·9

CHLOROFORM.

Urethane.		Acetanilid.		Naphthalene.		Acenapthene.		Chloral hydrate.	
0·0°	27·56	0·0°	3·24	0·0°	19·58	0·0°	12·72	0·0°	2·67
10·5°	42·66	10·6°	7·32	10·6°	23·14	11·2°	16·54	12·5°	4·23
17·4°	48·78	31·4°	15·64	30·3°	38·53	29·8°	54·62?	27·7°	31·93
31·1°	69·92	45·9°	24·07	52·5°	57·40	52·7°	42·19	44·0°	100·0
39·2°	78·54	61·4°	37·55					44·4°	100·0
								46·3°	100·0

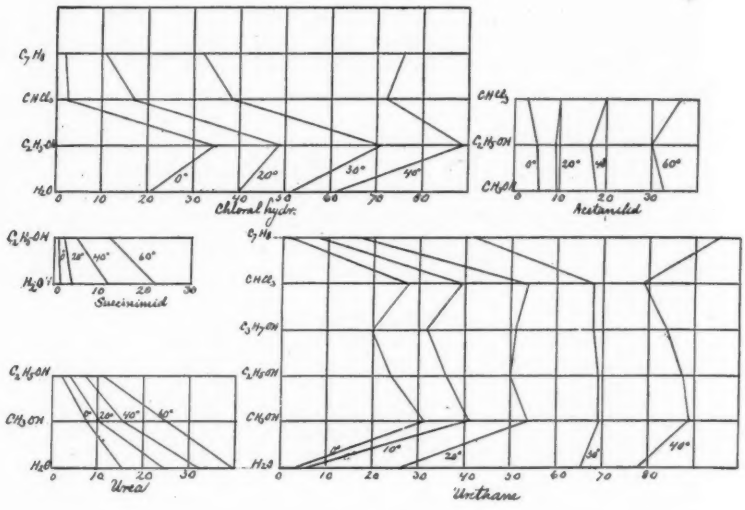
TOLUENE.

Urethane.		Naphthalene.		Acenaphthene.		Phenanthrene.		Chloral hydrate.	
0·0°	1·77	0·0°	12·82	0·0°	7·88	0·0°	11·88	0·0°	1·78
22·1°	19·63	25·2°	23·26	10·3°	10·76	13·9°	17·40	10·0°	4·24
33·9°	63·60	46·3°	47·37	24·1°	16·53	30·8°	26·90	20·7°	11·42
40·7°	87·86	69·5°	84·43	41·6°	29·29	54·9°	53·25	29·6°	31·18
				61·5°	45·08	78·3°	81·98	42·5°	89·86

It is unnecessary to plot these data, for with the exceptions of urethane in water and chloral hydrate in chloroform, the curves are quite regular. In the cases of urethane and chloral hydrate, the curves change direction very suddenly at about 12°, showing a very sudden decrease in solubility as the temperature decreases from this point.

Plots showing the variation in solubility as we pass from one solvent to another are perhaps of some interest. They are

2



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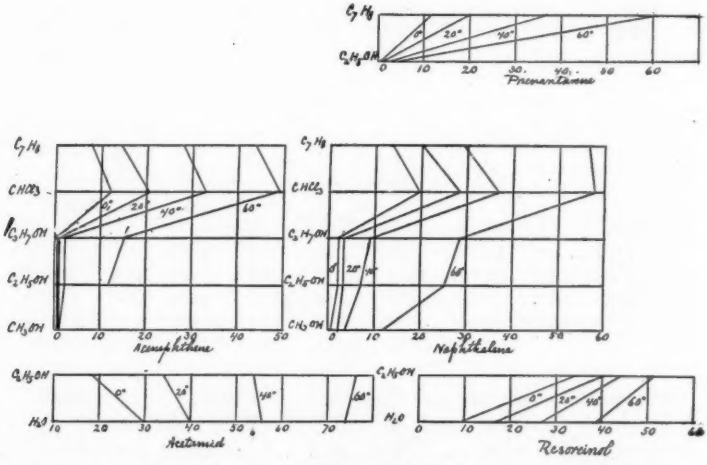


given in figures 2 and 3. The solubilities are expressed in percentage gram-molecules* along the horizontal line in that sol-

* According to the ordinary chemical formulæ.

vent whose formula is given at the commencement of the line. We notice that the relative solubility of a solute in several solvents can change very much with the temperature. For instance, acetamid is less soluble in alcohol than in water between 0° and about 50°, but above 50° it is more soluble in alcohol than in water. This is analogous to the relative changes in vapor pressures of some liquids. We notice the small increase in solubility of urethane in water as we pass from 0° to 10° and the rapid increase as we pass beyond that temperature. There seems to be some slight error in the solubility of the aqueous solution at 30°, but there is none at 10°, for the solubility at that temperature was determined twice. We notice also that there is no regularity in change of solubility as the molecular weights of the alcoholic solvents increase, whether we consider the molecular aggregations of the solutes† or not.

M. Schroeder‡ has deduced the equation

$$l\frac{n}{N+n} = A(t_o - t)$$

in which n is the number of gram-molecules of solvent in a saturated solution; A is a constant, the same for each solute whatever the solvent may be. t_o is the fusion temperature of the solute and t is the temperature of saturation. How this equation is obtained need not be considered. According to it, the curves of solubility of any solute in all solvents should coincide. Schroeder tested the equation with *p*-dibrombenzene in ethyl alcohol, propyl alcohol, isobutyl alcohol, ethyl ether, carbon disulphid, benzene, and brombenzene; with naphthalene in benzene. chlorbenzene, and carbon-tetrachloride; with *m*-dinitrobenzene in benzene, brombenzene, and chloroform. His results justify it, but mine do not; only for solutions of acenaphthene, naphthalene, and phenanthrene are the coincidences at all good.

The specific volumes of the solutions must be known before we can proceed to determine the osmotic pressures of the solutes, and therefore we now pass on to the densities.

These were easily obtained by sinking a pycnometer with a very small mouth into the saturated solution and drawing this in, the very small mouth keeping out particles of solute. Since the solution was kept stirred by air and contained an abundant excess of solute and since the temperature was kept constant for some ten minutes before drawing into the pycnometer, the solutions are to be considered in just the right

† This Journal, l. c.
‡ Zeitschr. Phys. Chemie, xi, 449, 1893.

condition, neither supersaturated nor undersaturated. The thermometer was the one used for the solubilities and the temperature is certain to 0·1°.

The uncertainty in the density is about 3 units in the third place in extreme cases; in general it is 2 or 3 units in the fourth place, the pycnometer holding between 8·5 and 9·8^{cc} and the weighings being made to milligrams.

The following tables give the temperatures and corresponding densities; namely, weights in grams reduced to vacuum of one cubic centimeter of solution.

WATER.

Urea.		Urethane.		Chloral hydrate.		Succinimid.	
0·0°	1·121	0·0°	1·023	0·0°	1·433	0·0°	1·025
19·0°	1·144	11·0°	1·035	15·3°	1·520	15·9°	1·043
32·2°	1·158	24·0°	1·073	31·0°	1·579	36·6°	1·111
46·3°	1·171	38·8°	1·064	46·6°	1·623	50·3°	1·140
64·5°	1·181	39·7°	1·065			65·0°	1·181
84·1°	1·196					84·4°	1·208

Acetamid.		Resorcinol.		Mannitol.	
0·0°	1·055	0·0°	1·101	0·0°	1·044
15·6°	1·046	14·4°	1·125	15·2°	1·050
31·6°	1·037	31·1°	1·149	31·1°	1·076
49·5°	1·022?	45·2°	1·161	47·7°	1·099
68·4°	1·011	63·4°	1·174	68·0°	1·148
		85·4°	1·179	85·9°	1·207

METHYL ALCOHOL.

Urea.		Urethane.		Acetanilid.	
0·0°	0·8612	0·0°	0·9565	0·0°	0·8602
17·4°	0·8674	15·5°	0·9902	16·7°	0·8698
29·7°	0·8764	28·2°	1·021	29·9°	0·8924
50·5°	0·9086	39·5°	1·044	43·9°	0·9206
66·8°	0·9534			61·7°	0·9596

Naphthalene.		Acenaphthene.		Methyl Alcohol (pure).	
0·0°	0·8194	0·0°	0·8133	0·0°	0·8110
16·6°	0·8088	12·5°	0·8030	18·3°	0·7938
29·0°	0·8048	31·6°	0·7900	29·4°	0·7834
47·0°	0·8086	45·6°	0·7823	46·2°	0·7675
61·7°	0·8436	64·1°	0·7843	59·8°	0·7540
68·0°	0·9022				

Ethyl Alcohol.

Urea.		Urethane.		Chloral hydrate.		Succinimid.		Acetamid.	
0·0°	0·8213	0·0°	0·8914	0·0°	1·110	0·0°	0·8150	0·0°	0·8562
15·7°	0·8113	14·1°	0·9443	16·7°	1·319	17·5°	0·8063	17·8°	0·8696
31·6°	0·8060	30·9°	1·004	33·5°	1·560	33·2°	0·8052	35·0°	0·8974
51·5°	0·8031	43·7°	1·044	40·8°	1·589	57·5°	0·8292	54·4°	0·9416
71·5°	0·8124					79·6°	0·9552	70·3°	0·9815
						80·6°	0·9563		

Resorcinol.		Benzamid.		Acetanilid.		p-Toluidin.		Naphthalene.	
0·0°	1·033	0·0°	0·8331	0·0°	0·8420	0·0°	0·8884	0·0°	0·8175
14·1°	1·036	14·1°	0·8328	17·2°	0·8472	15·6°	0·9168	17·0°	0·8104
36·1°	1·054	36·2°	0·8434	39·0°	0·8721	28·4°	0·9458	31·2°	0·8084
62·5°	1·077	57·2°	0·8754	58·1°	0·9156	40·6°	0·9636	51·0°	0·8230
81·4°	1·107	72·8°	0·9226	76·7°	0·9596			72·4°	0·9563
83·7°	1·112								

Phenanthrene.		Acenaphthene.		Ethyl alcohol (pure).	
0·0°	0·8141	0·0°	0·8108	0·0°	0·8074
15·6°	0·8035	15·0°	0·8013	19·1°	0·7921
35·3°	0·7960	36·3°	0·7910	35·3°	0·7780
52·2°	0·7941	53·4°	0·7890	52·3°	0·7633
76·4°	0·8654	73·0°	0·8186	72·8°	0·7448

Propyl Alcohol.

Urethane.		Naphthalene.		Acenaphthene.		Propyl alcohol (pure).	
0·0°	0·8798	0·0°	0·8285	0·0°	0·8228	0·0°	0·8192
13·3°	0·9156	14·6°	0·8228	12·9°	0·8171	18 0°	0·8067
29·1°	0·9804	30·7°	0·8206	26·6°	0·8110	28·0°	0·7991
42·1°	1·033	41·8°	0·8247	47·4°	0·8063	44·4°	0·7854
		59·7°	0·8634	64·7°	0·8217	65·1°	0·7678
		72·4°	0·9535	83·3°	0·9736	80·6°	0·7538

Chloroform.

Urethane.		Chloral hydrate.		Acetanilid.		p-Toluidin.	
0·0°	1·404	0·0°	1·529	0·0°	1·503	0·0°	1·278
16·4°	1·300	16·3°	1·505	19·1°	1·448	17·3°	1·168
31·2°	1·191	34·4°	1·565	34·2°	1·381	31·4°	1·066
43·4°	1·097	44·6°	1·615	47·3°	1·326	40·8°	0·9906
				62·4°	1·261		
				69·9°	1·227		

Naphthalene.		Acenaphthene.		Chloroform (pure).	
0·0°	1·393	0·0°	1·438	0·0°	1·526
20·2°	1·304	16·5°	1·378	18·2°	1·492
35·2°	1·230	29·1°	1·328	33·4°	1·464
53·2°	1·136	40·3°	1·281	44·6°	1·443
64·5°	1·072	55·8°	1·209	58·6°	1·417

TOLUENE.

Urethane.		Chloral hydrate.		p-Toluidin.		Naphthalene.	
0·0°	0·8872	0·0°	0·8978	0·0°	0·9110	0·0°	0·9124
18·4°	0·8792	18·5°	0·9328	16·6°	0·9228	17·9°	0·9130
34·0°	0·9570	28·4°	1·069	29·4°	0·9430	36·2°	0·9224
45·2°	1·042	40·8°	1·448	40·7°	0·9616	51·6°	0·9374
		42·0°	1·445			73·9°	0·9692

Phenanthrene.		Acenaphthene.		Toluene (pure).	
0·0°	0·9254	0·0°	0·9066	0·0°	0·8840
18·3°	0·9337	13·3°	0·9076	17·6°	0·8678
37·9°	0·9515	32·3°	0·9196	32·1°	0·8544
60·1°	0·9890	57·2°	0·9502	49·8°	0·8381
86·3°	1·038	83·5°	1·006	65·9°	0·8232
				85·0°	0·8048

Of these solutions, so far as they could be examined, only the following contain solutes with normal molecular weights.*

Urea	in	water	at 32° to 41°	
"	"	methyl alcohol	" 28°	
"	"	ethyl "	" 27°	
Acetanilid	"	methyl "	" 31°(?)	
"	"	ethyl "	" 21° to 42°	
Naphthalene	"	" "	" 28° " 45°	
"	"	toluene "	" 29° " 45°	
Acenaphthene	"	propyl alcohol	" 45°(?)	
"	"	toluene	" 21° to 51°	

Selecting 27° as the temperature and taking solubilities at that temperature from solubility curves and densities from density curves, we get the following table:

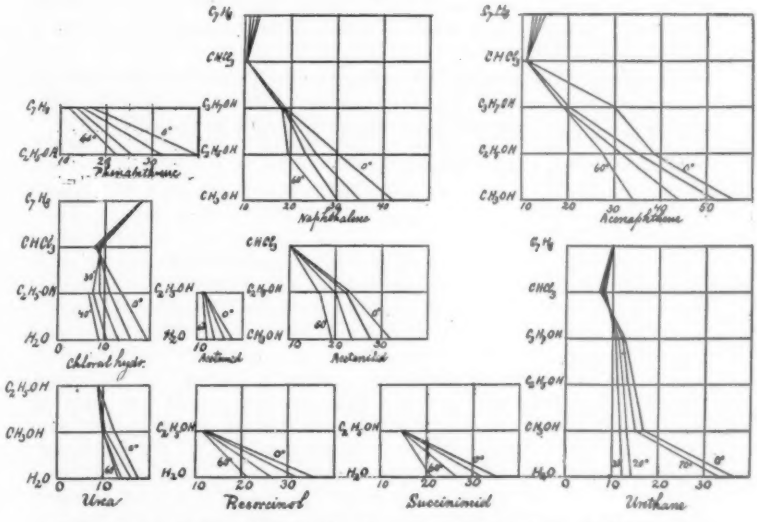
Solution.	Solubility.		Density.	Osmotic Pressure.	
Urea in water	26	grmmols	1·155	10·4	atmos.
" methyl alcohol	12	"	0·873	3·0	"
" ethyl "	5	"	0·805	0·9	"
Acetanilid in methyl alcohol	12	"	0·891	2·4	"
" ethyl "	11	"	0·858	1·7	"
Naphthalene in ethyl alcohol	4	"	0·810	0·7	"
" " toluene	25	"	0·918	2·3	"
Acenaphthene in propyl alcoh'l	1	"	0·810	0·1	"
" toluene	18	"	0·918	1·7	"

The osmotic pressure is not at all constant for each solute, and we see that the undissolved solute does not balance the dissolved solute to an equal extent in each solvent though the molecular weights of the solutes are simple. So the analogy of solution to vaporization is seen to be far from complete.

* This Journal, l. c.

In conclusion a few words about the densities and molecular volumes. There is no need of putting the data given above into plots. There is no peculiarity in any of them, not even in the aqueous solution of urethane nor in the chloroform solution of chloral hydrate, but the plots showing variation in molecular volume as a solute passes from one solvent into another are instructive. They are given in figure 4.

4



The formula at the beginning of the horizontal line gives the solvent, and the numbers along the horizontal give the relative volumes of one gram-molecule of solute at the temperature stated on the lines.

For example, the relative volume of one gram-molecule of acenaphthene in chloroform at 10° has been obtained in this way:—

Solubility of acenaphthene from solubility curve=16·0% gram-mols.

Proportion of chloroform=84·0 • 119·3/ (84·0 • 119·3 + 16·0 • 154).

Volume of one gram chloroform at 10° from density curve= 1/1·51cc.

" " chloroform in one gram of solution is [84·0 • 119·3/ (84·0 • 119·3 + 16·0 • 154)] 1/1·51cc=0·5327cc.

" " one gram of solution at 10°=1/1·40cc.

" " acenaphthene in one gram of solution=1/1·40—0·5327 =0·1811cc.

" corresponding to one molecule of acenaphthene=0·1811/16 =0·0113.

For convenience, the values are all multiplied by 1000 before plotting.

We notice the following:—

The molecular volumes of the solutes are larger in water than in the other solvents and decrease in the order of methyl alcohol, ethyl alcohol, propyl alcohol, toluene and chloroform, the only exception being perhaps choral hydrate in ethyl alcohol compared to its solution in chloroform.

The molecular volumes in chloroform show decided constancy for every temperature and concentration observed, and to a lesser extent in toluene.

In general, the molecular volumes of the solutes decrease as the temperature rises and the concentration increases. The exceptions are urethane and chloral hydrate in chloroform.

Rutgers College, April, 1897–June, 1902.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Radio-active Bismuth.*—Polonium, the radio-active substance occurring with bismuth in pitchblende, was the first of these substances discovered (by Mr. and Mrs. Curie). Subsequent investigations by Giesel led the latter to believe that polonium was nothing more than bismuth made active by induction. Marckwald, however, has recently obtained results which indicate that polonium is a distinct element. From a by-product obtained from pitchblende, by the usual methods, bismuth oxychloride was prepared which was strongly radio-active, and which showed no decrease in activity after several months. Upon subjecting a solution of this substance to electrolysis, it was found that the metal which was deposited at first displayed much greater activity than the final product. This result led to the attempt to precipitate polonium, from hydrochloric acid solutions of the oxychloride, by means of a polished stick of metallic bismuth. As a result, the metal became coated immediately with a fine black deposit, which gradually increased, and when it had been removed from the solution and washed, it showed a surprisingly strong effect on the electroscope. At the distance of a decimeter the leaves of the charged electroscope collapsed in a moment, and even a gutta-percha rod which had been well rubbed with fur was immediately discharged upon the approach of the bismuth stick. The important fact was noticed that metallic bismuth is thus able to remove practically all of the active material from a solution. The powder could be scraped from the bismuth rod, and the amount thus obtained from 8^g of bismuth oxychloride was about 5^{mg}. From this result it was calculated that a ton of pitchblende would contain not more than one gram of the substance. The powder was found not to be a pure metal, but to contain some chlorine. Upon heating, a small portion volatilized, probably as chloride, and the residue fused to a white, exceedingly brittle, metallic bead. This was soluble in nitric acid, and the solution, as far as it could be tested, gave reactions for bismuth. The salts are as strongly active as the metal, and the rays are characteristically different from those of radium in being unable to penetrate any intervening substance. Even a piece of filter-paper wrapped around a stick of bismuth coated with the active metal causes it to lose all its effect. The experiments are to be continued with larger quantities of material, and it is hoped that an atomic weight determination may be made.—*Berichte*, xxxv, 365. H. L. W.

2. *A Thermochemical Constant.*—F. W. Clarke, in a preliminary paper, has made a generalization from a consideration of Thomsen's work on the heats of combustion of certain organic compounds. In the first place, he has re-calculated Thomsen's

results so that they represent the formation of gaseous instead of liquid water. He then finds for the aliphatic hydrocarbons and their non-oxygenated derivatives that $\frac{4K}{12a+6b-c-8n}$ is a constant, where K represents the heat of combustion of the compound, a the number of molecules of CO_2 produced, b the number of molecules of H_2O, c the number of oxygen molecules involved, and n the number of atomic unions or linkings in the compound burned. In fixing the value of n, double and triple linkings are not distinguished from simple ones, so that for all chain molecules n is equivalent to the number of atoms minus one. The coefficients 4, 12, 6, 1 and 8 appear to have been chosen arbitrarily, but the results obtained with them in the cases of fourteen hydrocarbons are remarkably uniform, and the author evidently considers it important that the constant, which averages 13,873 in this case, is very near the neutralization constant of acids and bases, which is 13,700 calories. The same uniform constant was obtained with many other organic compounds by modifying the formula in accordance with the presence of several other elements: thus for halogen compounds were used the formulas $\frac{4K}{12a+6b+h-c-8n}$, $\frac{4K}{12a+6b+2h_1-c-8n}$ and $\frac{4K}{12a+6b+4h_2-c-8n}$, where h, h_1 and h_2 represent the numbers of chlorine, bromine and iodine molecules, supposed by the author to be formed by the complete combustion of the halides. For nitrogen compounds two formulas were used; for cyanides and nitrites, where m represents the number of nitrogen molecules set free, the divisor is $12a+6b+3m-c-8m$, while for amines $3m$ is replaced by $9m$. For sulphur compounds the term $9s$ is introduced, while c_1, the number of oxygen molecules present in the compound, is subtracted when the latter element is present. In this way conformable results were obtained with nineteen halogen compounds, four cyanides, ten amines, eight sulphur compounds, and eleven alcohols. The ring compounds have not yet been worked out in this way, and there are a few substances in most of the groups which fail to give the usual result. A consideration of the exceptions is deferred until the complete memoir is published. The conclusion is reached that, in any class of compounds, the heat of formation is proportional to the number of atomic linkings within the molecule, and seems to bear no relation to the masses of the atoms which are combined.

It is to be hoped that Professor Clarke has discovered a new and important thermochemical law, but from the arbitrary nature of the formulas used the suspicion arises that the law may be a very obscure one.—*Jour. Amer. Chem. Soc.*, xxiv, 882. H. L. W.

3. *The Heatless Condition of Matter.*—In the June number of this Journal mention was made of Brinkworth and Martin's theory that pressure may be able to prevent molecular vibration

and thus cause matter to assume a condition which is devoid of heat. In regard to that notice the editor has received from one of the authors a letter which is too long to be inserted, but which should be acknowledged here. It does not appear that objection is made to our presentation of the main points of the theory, but in relation to our opening remark, "Brinkworth and Martin, with apparent seriousness, have made a curious extension of the kinetic theory," the letter says, "Your abstractor appeared to doubt the seriousness of the paper. I write at once to say that in this matter we are in deadly earnest." The fact is, we intended to convey the idea that the seriousness of the article impressed us. Objection is made to our opinion that "Their deductions are based upon an entirely unproven assumption," and, in this connection, the letter refers to some points which are to be brought out in a future article. It seems to us that no injustice has been done to the authors as far as their preliminary publication is concerned, and that further discussion of their theory should be postponed until their more elaborate paper has appeared. H. L. W.

4. *Elementary Chemistry*, by F. W. CLARKE and L. M. DENNIS. 12mo. Pp. 340. New York, 1902 (American Book Company).—In preparing this little text-book the authors have aimed especially to make it a means of training in the interpretation of evidence. Each generalization is made to follow the evidence upon which it rests. The work is accompanied by a laboratory manual, but a reasonable number of experiments, nearly all of which are of the simplest character, are described throughout the text. The book appears less dry and more interesting than most of the works on the subject on account of the constant attention which is paid to the application of chemistry to human affairs and its utility in modern life. The authors have done no more with the theory of ionization than to give it a very brief mention. Although they consider this theory unsuitable for discussion in a work of this kind, it seems probable that its use in a simple manner would present no more difficulty to the beginner than some of the theories which are introduced. It is satisfactory to notice that the book contains a short treatise (about 60 pages) on organic chemistry, a subject which is too often omitted in books on elementary chemistry. Very few things have been noticed in the work which seem unsatisfactory, but it appears that the somewhat imaginary structural formula for the double sulphate of magnesium and potassium (p. 202) is hardly appropriate in such a book, and objection may be made to the equation $KClO_3 = KCl + O_3$, because O_3 is ozone. A mistake is made in characterizing lithium as the lightest solid known, for solid hydrogen is mentioned in the book. H. L. W.

5. *Liquid Hydrogen and Helium;* from the inaugural address delivered at Belfast by Prof. JAMES DEWAR, President of the British Association.—* * * From this speculative divergency it is clear no definite conclusion could be reached regarding the physical prop-

erties of liquid or solid hydrogen, and the only way to arrive at the truth was to prosecute low-temperature research until success attended the efforts to produce its liquefaction. This result I definitely obtained in 1898. The case of liquid hydrogen is, in fact, an excellent illustration of the truth already referred to, that no theoretical forecast, however apparently justified by analogy, can be finally accepted as true until confirmed by actual experiment. Liquid hydrogen is a colorless, transparent body of extraordinary intrinsic interest. It has a clearly defined surface, is easily seen, drops well, in spite of the fact that its surface tension is only the thirty-fifth part of that of water or about one-fifth that of liquid air, and can be poured easily from vessel to vessel. The liquid does not conduct electricity, and, if anything, is slightly diamagnetic. Compared with an equal volume of liquid air, it requires only one-fifth the quantity of heat for vaporization; on the other hand, its specific heat is ten times that of liquid air or five times that of water. The coefficient of expansion of the fluid is remarkable, being about ten times that of gas; it is by far the lightest liquid known to exist, its density being only one-fourteenth that of water; the lightest liquid previously known was liquid marsh gas, which is six times heavier. The only solid which has so small density as to float upon its surface is a piece of pith wood. It is by far the coldest liquid known. At ordinary atmospheric pressure it boils at *minus* 252·5 degrees or 20·5 degrees absolute. The critical point of the liquid is about 29 degrees absolute and the critical pressure not more than fifteen atmospheres. The vapor of the hydrogen arising from the liquid has nearly the density of air—that is, it is fourteen times that of the gas at the ordinary temperature. Reduction of the pressure by an air-pump brings down the temperature to *minus* 258 degrees, when the liquid becomes a solid resembling frozen foam, and this by further exhaustion is cooled to *minus* 260 degrees, or 13 degrees absolute, which is the lowest steady temperature that has been reached. The solid may also be got in the form of a clear, transparent ice, melting at about 15 degrees absolute, under a pressure of 55^{mm}, possessing the unique density of one-eleventh that of water. Such cold involves the solidification of every gaseous substance but one that is at present definitely known to the chemist, and so liquid hydrogen introduces the investigator to a world of solid bodies. The contrast between this refrigerating substance and liquid air is most remarkable. On the removal of the loose plug of cotton-wool used to cover the mouth of the vacuum vessel in which it is stored, the action is followed by a miniature snow-storm of solid air, formed by the freezing of the atmosphere at the point where it comes into contact with the cold vapor rising from the liquid. This solid air falls into the vessel and accumulates as a white snow at the bottom of the liquid hydrogen. When the outside of an ordinary test-tube is cooled by immersion in the liquid, it is soon observed to fill up with solid air, and if the tube be now lifted out a

double effect is visible, for liquid air is produced both in the inside and on the outside of the tube—in the one case by the melting of the solid, and in the other by condensation from the atmosphere. A tuft of cotton-wool soaked in the liquid and then held near the pole of a strong magnet is attracted, and it might be inferred therefrom that liquid hydrogen is a magnetic body. This, however, is not the case: the attraction is due neither to the cotton-wool nor to the hydrogen—which indeed evaporates almost as soon as the tuft is taken out of the liquid—but to the oxygen of the air, which is well known to be a magnetic body, frozen in the wool by the extreme cold.

The strong condensing powers of liquid hydrogen afford a simple means of producing vacua of very high tenuity. When one end of a sealed tube containing ordinary air is placed for a short time in the liquid, the contained air accumulates as a solid at the bottom, while the higher part is almost entirely deprived of particles of gas. So perfect is the vacuum thus formed, that the electric discharge can be made to pass only with the greatest difficulty. Another important application of liquid air, liquid hydrogen, etc., is as analytic agents. Thus, if a gaseous mixture be cooled by means of liquid oxygen, only those constituents will be left in the gaseous state which are less condensable than oxygen. Similarly, if this gaseous residue be in its turn cooled in liquid hydrogen, a still further separation will be effected, everything that is less volatile than hydrogen being condensed to a liquid or solid. By proceeding in this fashion it has been found possible to isolate helium from a mixture in which it is present to the extent of only one part in one thousand. By the evaporation of solid hydrogen under the air-pump we can reach within 13 or 14 degrees of the zero, but there or thereabouts our progress is barred. This gap of 13 degrees might seem at first insignificant in comparison with the hundreds that have already been conquered. But to win one degree low down the scale is quite a different matter from doing so at higher temperatures; in fact, to annihilate these few remaining degrees would be a far greater achievement than any so far accomplished in low-temperature research. For the difficulty is twofold, having to do partly with process and partly with material. The application of the methods used in the liquefaction of gases becomes continually harder and more troublesome as the working temperature is reduced; thus, to pass from liquid air to liquid hydrogen —a difference of 60 degrees—is, from a thermodynamic point of view, as difficult as to bridge the gap of 150 degrees that separates liquid chlorine and liquid air. By the use of a new liquid gas exceeding hydrogen in volatility to the same extent as hydrogen does nitrogen, the investigator might get to within five degrees of the zero; but even a second hypothetical substance, again exceeding the first one in volatility to an equal extent, would not suffice to bring him quite to the point of his ambition. That the zero will ever be reached by man is

extremely improbable. A thermometer introduced into regions outside the uttermost confines of the earth's atmosphere might approach the absolute zero, provided that its parts were highly transparent to all kinds of radiation, otherwise it would be affected by the radiation of the sun, and would therefore become heated. But supposing all difficulties to be overcome, and the experimenter to be able to reach within a few degrees of the zero, it is by no means certain that he would find the near approach of the death of matter sometimes pictured. Any forecast of the phenomena that would be seen must be based on the assumption that there is continuity between the processes studied at attainable temperatures and those which take place at still lower ones. Is such an assumption justified? It is true that many changes in the properties of substances have been found to vary steadily with the degree of cold to which they are exposed. But it would be rash to take for granted that the changes which have been traced in explored regions continue to the same extent and in the same direction in those which are as yet unexplored. Of such a breakdown low-temperature research has already yielded a direct proof at least in one case. A series of experiments with pure metals showed that their electrical resistance gradually decreases as they are cooled to lower and lower temperatures, in such ratio that it appeared probable that at the zero of absolute temperature they would have no resistance at all and would become perfect conductors of electricity. This was the inference that seemed justifiable by observations taken at depths of cold which can be obtained by means of liquid air and less powerful refrigerants. But with the advent of the more powerful refrigerant liquid hydrogen it became necessary to revise that conclusion. A discrepancy was first observed when a platinum resistance thermometer was used to ascertain the temperature of that liquid boiling under atmospheric and reduced pressure. All known liquids, when forced to evaporate quickly by being placed in the exhausted receiver of an air-pump, undergo a reduction in temperature, but when hydrogen was treated in this way it appeared to be an exception. The resistance thermometer showed no reduction as was expected, and it became a question whether it was the hydrogen or the thermometer that was behaving abnormally. Ultimately, by the adoption of other thermometrical appliances, the temperature of the hydrogen was proved to be lowered by exhaustion as theory indicated. Hence it was the platinum thermometer which had broken down ; in other words, the electrical resistance of the metal employed in its construction was not, at temperatures about *minus* 250° C., decreased by cold in the same proportion as at temperatures about *minus* 200°. This being the case, there is no longer any reason to suppose that at the absolute zero platinum would become a perfect conductor of electricity ; and in view of the similarity between the behavior of platinum and that of other pure metals in respect of temperature and conductivity, the presumption is that the same is true of

them also. At any rate, the knowledge that in the case of at least one property of matter we have succeeded in attaining a depth of cold sufficient to bring about unexpected change in the law expressing the variation of that property with temperature, is sufficient to show the necessity for extreme caution in extending our inferences regarding the properties of matter near the zero of temperature. Lord Kelvin evidently anticipates the possibility of more remarkable electrical properties being met with in the metals near the zero. A theoretical investigation on the relation of "electrions" and atoms has led him to suggest a hypothetical metal having the following remarkable properties: below 1 degree absolute it is a perfect insulator of electricity, at 2 degrees it shows noticeable conductivity, and at 6 degrees it possesses high conductivity. It may safely be predicted that liquid hydrogen will be the means by which many obscure problems of physics and chemistry will ultimately be solved, so that the liquefaction of the last of the old permanent gases is as pregnant now with future consequences of great scientific moment as was the liquefaction of chlorine in the early years of the last century.

The next step towards the absolute zero is to find another gas more volatile than hydrogen, and that we possess in the gas occurring in cleveite, identified by Ramsay as helium, a gas which is widely distributed, like hydrogen, in the sun, stars and nebulæ. A specimen of this gas was subjected by Olszewski to liquid air temperatures, combined with compression and subsequent expansion, following the Cailletet method, and resulted in his being unable to discover any appearance of liquefaction, even in the form of mist. His experiments led him to infer that the boiling-point of the substance is probably below 9 degrees absolute. After Lord Rayleigh had found a new source of helium in the gases which are derived from the Bath springs, and liquid hydrogen became available as a cooling agent, a specimen of helium cooled in liquid hydrogen showed the formation of fluid, but this turned out to be owing to the presence of an unknown admixture of other gases. As a matter of fact, a year before the date of this experiment I had recorded indications of the presence of unknown gases in the spectrum of helium derived from this source. When subsequently such condensable constituents were removed, the purified helium showed no signs of liquefaction, even when compressed to 80 atmospheres, while the tube containing it was surrounded with solid hydrogen. Further, on suddenly expanding, no instantaneous mist appeared. Thus helium was definitely proved to be a much more volatile substance than hydrogen in either the liquid or solid condition. The inference to be drawn from the adiabatic expansion effected under the circumstances is that helium must have touched a temperature of from 9 to 10 degrees for a short time without showing any signs of liquefaction, and consequently that the critical point must be still lower. This would force us to anticipate that the boiling-point of the liquid will be about 5 degrees absolute, or liquid

helium will be four times more volatile than liquid hydrogen, just as liquid hydrogen is four times more volatile than liquid air. Although the liquefaction of the gas is a problem for the future, this does not prevent us from safely anticipating some of the properties of the fluid body. It would be twice as dense as liquid hydrogen, with a critical pressure of only 4 or 5 atmospheres. The liquid would possess a very feeble surface-tension, and its compressibility and expansibility would be about four times that of liquid hydrogen, while the heat required to vaporize the molecule would be about one-fourth that of liquid hydrogen. Heating the liquid 1 degree above its boiling-point would raise the pressure $1\frac{3}{4}$ atmospheres, which is more than four times the increment for liquid hydrogen. The liquid would be only seventeen times denser than its vapor, whereas liquid hydrogen is sixty-five times denser than the gas it gives off. Only some 3 or 4 degrees would separate the critical temperature from the boiling-point and the melting-point, whereas in liquid hydrogen the separation is respectively 10 and 15 degrees. As the liquid refractivities for oxygen, nitrogen and hydrogen are closely proportional to the gaseous values, and as Lord Rayleigh has shown that helium has only one-fourth the refractivity of hydrogen, although it is twice as dense, we must infer that the refractivity of liquid helium would also be about one-fourth that of liquid hydrogen. Now hydrogen has the smallest refractivity of any known liquid, and yet liquid helium will have only about one-fourth of this value—comparable, in fact, with liquid hydrogen just below its critical point. This means that the liquid will be quite exceptional in its optical properties, and very difficult to see. This may be the explanation of why no mist has been seen on its adiabatic expansion from the lowest temperatures. Taking all these remarkable properties of the liquid into consideration, one is afraid to predict that we are at present able to cope with the difficulties involved in its production and collection. Provided the critical point is, however, not below 8 degrees absolute, then from the knowledge of the conditions that are successful in producing a change of state in hydrogen through the use of liquid air, we may safely predict that helium can be liquefied by following similar methods. If, however, the critical point is as low as 6 degrees absolute, then it would be almost hopeless to anticipate success by adopting the process that works so well with hydrogen. The present anticipation is that the gas will succumb after being subjected to this process, only, instead of liquid air under exhaustion being used as the primary cooling agent, liquid hydrogen evaporating under similar circumstances must be employed. In this case, the resulting liquid would require to be collected in a vacuum vessel the outer walls of which are immersed in liquid hydrogen. The practical difficulties and the cost of the operation will be very great; but, on the other hand, the descent to a temperature within 5 degrees of the zero would open out new vistas of scientific inquiry, which would add immensely to our

knowledge of the properties of matter. To command in our laboratories a temperature which would be equivalent to that which a comet might reach at an infinite distance from the sun would indeed be a great triumph for science. If the present Royal Institution attack on helium should fail. then we must ultimately succeed by adopting a process based on the mechanical production of cold through the performance of external work. When a turbine can be worked by compressed helium, the whole of the mechanism and circuits being kept surrounded with liquid hydrogen, then we need hardly doubt that the liquefaction will be effected. In all probability gases other than helium will be discovered of greater volatility than hydrogen. It was at the British Association Meeting in 1896 that I made the first suggestion of the probable existence of an unknown element which would be found to fill up the gap between argon and helium, and this anticipation was soon taken up by others and ultimately confirmed. Later, in the Bakerian Lecture for 1901, I was led to infer that another member of the helium group might exist having the atomic weight about 2, and this would give us a gas still more volatile, with which the absolute zero might be still more nearly approached. It is to be hoped that some such element or elements may yet be isolated and identified as coronium or nebulium. If amongst the unknown gases possessing a very low critical point some have a high critical pressure instead of a low one, which ordinary experience would lead us to anticipate, then such difficultly liquefiable gases would produce fluids having different physical properties from any of those with which we are acquainted. Again, gases may exist having smaller atomic weights and densities than hydrogen, yet all such gases must, according to our present views of the gaseous state, be capable of liquefaction before the zero of temperature is reached. The chemists of the future will find ample scope for investigation within the apparently limited range of temperature which separates solid hydrogen from the zero. Indeed, great as is the sentimental interest attached to the liquefaction of these refractory gases, the importance of the achievement lies rather in the fact that it opens out new fields of research and enormously widens the horizon of physical science, enabling the natural philosopher to study the properties and behavior of matter under entirely novel conditions. This department of inquiry is as yet only in its infancy, but speedy and extensive developments may be looked for, since within recent years several special cryogenic laboratories have been established for the prosecution of such researches, and a liquid-air plant is becoming a common adjunct to the equipment of the ordinary laboratory.—*Nature, Sept. 11, 1902.*

6. *Vapor-pressures of Liquid Oxygen and of Liquid Hydrogen.*—In an abstract of a paper by M. W. TRAVERS, G. SENTER and A. JAQUEROD read before the Royal Society on June 19 (Nature, vol. lxvi, p. 382), the results contained in the following table are given :

Vapor Pressures.

	Liquid Oxygen.		Liquid Hydrogen.	
Pressure in mm.	Temp. on hydrogen scale.	Temp. on helium scale.	Temp. on hydrogen scale.	Temp. on helium scale.
	°	°	°	°
800	90·60	90·70	20·41	20·60
760	90·10	90·20	20·22	20·41
700	89·33	89·43	19·93	20·12
600	87·91	88·01	19·41	19·61
500	86·29	86·39	18·82	19·03
400	84·39	84·49	18·15	18·35
300	82·09	82·19	17·36	17·57
200	79·07	79·17	16·37	16·57
100	- --	----	14·93	15·13
50	----	----	----	14·11

The authors add, in conclusion :

"Though the pressure coefficients of hydrogen and helium between 0° and 100° C. show no appreciable difference, measurements of low temperatures on the scales of the two thermometers are not identical. It is probable that at the normal temperature both gases may be considered as so nearly perfect that the difference between the gas scale and the absolute scale is insignificant. As the critical point of helium lies much lower than that of hydrogen, measurements of low temperatures on the helium scale should approach more closely to absolute temperatures than measurements on the hydrogen scale. It is pointed out that helium should replace hydrogen as the normal thermometric substance.

The melting point of hydrogen was found to be 14°·10 on the helium scale.

The pure helium used in the thermometric measurements was obtained by passing purified cleveite gas through a coil cooled to 15° in liquid hydrogen boiling *in vacuo*. An unsuccessful attempt was made to liquefy this gas, which could not be condensed at 13° under a pressure of 60 atmospheres.

The vapor pressures of solid neon were measured at temperatures corresponding to 20°·4 (12·8^{mm}) and 15°·65 (2·4^{mm}). It was shown that the vapor pressure did not change as the solid evaporated, proving that neon is a homogeneous substance."

II. Geology and Mineralogy.

1. *Martinique.*—The July issue of the *National Geographic Magazine* is called the "Martinique number," and is devoted to descriptions and discussions of the volcanic eruption of Mt. Pelée which began in May last, together with some references to the contemporaneous eruption of La Soufrière on the island of St. Vincent. The number is of double the usual size and is a valuable contribution to the study of the recent eruptions in the Lesser Antilles, containing as it does the reports of Robert T. Hill, of the United States Geological Survey, and Israel C. Russell, of the University of Michigan, two of the representa-

tives commissioned by the National Geographic Society to investigate the phenomena attending the cataclysms. The number is enriched by the notes by J. S. Diller on the volcanic rocks collected by Hill and Russell; by a chemical discussion by W. F. Hillebrand of analyses of ejecta from the two islands, and by a compilation by James Page of the reports of vessels as to the area over which the dust from the eruptions was distributed. The number is well illustrated with four maps and nineteen photographs. Fourteen of the latter are from excellent negatives taken by Russell.

Hill's report opens with a brief general statement of the geography and geology of the whole chain of the Windward Islands or Lesser Antilles, which are almost entirely volcanic in character, with the exception of Barbados. He holds that the volcanoes of these islands date back to Eocene time, at least; that the greater masses of the present volcanic heights were piled up before the Pliocene, and that "the present craters are merely secondary and expiring phenomena." In discussing the present eruption, after relating the premonitory events of the preceding fortnight, Hill gives in detail the history of the great outburst of May 8 as derived from the accounts of eyewitnesses, and then elaborates his personal observations, which were made between May 21 and 30. He holds that the eruption which destroyed St. Pierre came from a crater low down on the southwest slope of Mt. Pelée, two miles from the northern limit of the city and a mile and a half from the sea, which he calls the "Soufrière" or "Étang Sec" crater. He considers the mud-flows to be primary phenomena of the eruption and to have come from this crater and from several "mud-craters" on the slopes of the mountain, the sites of some of which had long been known as thermal springs.

Hill calculates that only 12·5 square miles, or one-twentieth of the total area of Martinique, have been seriously affected by the eruption. No great geological changes have been brought about, but the configuration of the summit and the outline of the seacoast have been changed somewhat. He says, "There have been no lava flows whatsoever. . . . No true bombs have been ejected or molten rock in any form." His conclusion is that conflagration and death in St. Pierre may ultimately be explained by either of two theories:

(1.) The heat-blast theory. This hypothesis assumes that the lapilli, gases, and steam of the ejected cloud were sufficiently hot to have inflamed the city and destroyed the people by singeing, suffocation, and asphyxiation. It does not account for the forces exerted radially and horizontally, nor for the flame.

(2.) The aërial-explosion theory. The explosion of gases within the erupted cloud after their projection into the air would account for all the phenomena observed.

Russell's report takes the form of a letter to the Society. He does not subscribe to the opinion that the inhabitants of St. Pierre were asphyxiated by noxious gases or killed by a gas explosion.

He holds that the general cause of death and destruction was a blast of steam charged with hot dust, which passed through the city with hurricane force, and that gases, probably in part inflammable, were present, but played only a secondary part in the disaster.

Most of Russell's report is devoted to St. Vincent. He holds that the destruction on this island was due to dust, lapilli and stones which fell on the land while yet hot; but that a hurricane blast of steam charged with burning dust did not sweep down from La Soufrière as it did from Mt. Pelée. The area of devastation on St. Vincent was much greater than on Martinique. Attention is called to the violent secondary or superficial eruptions due to rain or river water coming into contact with the still heated interior of the great deposits of recent ash in the gorges of the Wallibou and Dry Rivers; to the pulsating flow of the Wallibou river due to overloading by volcanic sand; to the canyon-like dendritic drainage forms already produced in the coating of fresh dust and lapilli by the rains; and to the fact that houses standing on the windward (east) slope of the volcano had suffered most on the sides farthest from the crater.

Five miles from the crater Russell found the level fields coated with a layer of new volcanic débris about two feet thick. This would be a minimum measure and the average thickness of the deposit would be several times as great. The greater part of the débris consists of gray scoriaceous andesite and came from the columns of fresh lava that rose in the conduit of La Soufrière. This material was sufficiently cooled to become solid before it was blown into the air, and to a great extent was reduced to dust by the sudden expansion of the steam it contained. In addition to the fragments of fresh lava the fields were strewn with angular masses of older and much more compact lavas torn from the throat of the volcano.

Diller describes the older lavas of Martinique, collected by Hill, as being hypersthene andesite, hornblende-hypersthene andesite, hornblende andesite and dacite (quartz andesite), and the products of the May eruption of Mt. Pelée as belonging to the hypersthene-andesite class. He says that the specimens from St. Vincent are of hypersthene andesites, remarkable for their content of olivine.

Hillebrand concludes that, while the ejecta from the two volcanoes are of the same general type, and while the material from the same vent may vary in composition within limits, according as it is collected near to or far from the vent, and in coherent or finely divided form, yet there are characteristic differences by which it appears easy to distinguish the product of one volcano from that of the other. Diller's report is accompanied by seven analyses of pumice, sand and dust from these eruptions and Hillebrand's discussion by three such analyses. E. O. H.

2. *The Report of the Geological Survey of Louisiana:* G. D. Harris, A. C. Veatch, J. Pacheco.—The papers contained in

this report are of especial economic value to this and neighboring States, including as they do reports on the "Salines of North Louisiana," A. C. Veatch, "Subterranean Waters of Louisiana" and "Oil in Louisiana," by G. D. Harris.

The map of the Mississippi Embayment shows the Jackson Stage for the first time with its most probable northern distribution. The statement with regard to the close of the Cretaceous is of interest at this time because of its importance to the oil industry: "In Louisiana we have reason to believe that the raising and depression of the Cretaceous beds was of a much more violent nature [than farther north], that folds and faults were numerous and on a large scale and a great irregularity of surface feature characterized the newly formed rocks." Professor Harris differs from R. T. Hill and others who believe that there are no "structural complications" in this formation.

Doubt is thrown on the usually accepted theory concerning the origin of the "Mud Lumps" of the Mississippi. No new theory is advanced, but the statement is made that, "that they rise in domes or anticlines and preserve their regular bedding is proven by their structure." "So far as we observed, none were formed as volcano-like cones."

The report on the Salines of North Louisiana, A. C. Veatch, contains a history of the early operations of the various salt wells and licks together with well sections and a discussion of the geology. It is shown that "the principal brine springs are to be regarded as Cretaceous outcrops." The dome structure of these and other north Louisiana Cretaceous outcrops is accepted. The maps of this report and of Reports III and IV are excellent.

The Reports on the Geography and Geology of the Sabine and Ouachita Rivers contain discussions and explanations of the "landslip islands" of the Ouachita River and the shoals of the Sabine River which are of especial interest to physiographers.

One of the most valuable reports, economically, is that on the Subterranean Waters of Louisiana.

It is to be regretted that a volume containing so much valuable matter and so well illustrated by maps and half-tones is not printed on better paper and bound more substantially.

3. *Die Alpen im Eiszeitalter;* von ALBRECHT PENCK und EDUARD BRÜCKNER. Parts 1 and 2. 224 pp., with many charts and figures. Leipzig. (Tauchnitz.)—After fourteen years of investigation Professors Penck and Brückner have begun the publication of their views regarding glaciation in the Alps. The completed work will consist of about six parts, dealing with the entire Alpine system throughout the Pleistocene with especial reference to the topography resulting from ice action. In the two parts already issued Professor Penck discusses the general character of glaciers and of glacial deposits, and explains with great detail the glacial phenomena of the northern and eastern Alpine border region, particularly the area between the Iller and the Lech.

4. *Bacubirito, the Great Meteorite of Sinaloa, Mexico.*—An interesting account is given in vol. iv (pp. 67–74) of the Proceedings of the Rochester Academy of Science, by HENRY A. WARD, of a visit to the gigantic mass of meteoric iron discovered in 1876 in the State of Sinaloa, Mexico. This is perhaps the largest of all known meteorites; its weight is roughly estimated at 50 tons, and its only rival is the meteorite of Anighito, Greenland, to which a recent estimate has assigned a weight of 46⅓ tons. The three meteorites most nearly approaching these are those of Bemdego, Brazil, 5⅛ tons; of San Gregorio, Mexico, 11½ tons, and Chupaderos, Mexico, 15⅔ tons. The dimensions of the Bacubirito meteorite were measured, after extensive excavations of the soil in which it was nearly imbedded, as follows: length, 13 feet 1 inch; width 6 feet 2 inches; thickness, 5 feet 4 inches. The shape is extremely irregular, being compared to that of a ham; the cubic contents consequently could be only approximately estimated. In composition, an analysis by Whitfield has shown it to contain about 7 per cent nickel, and its structure is eminently octahedral. The exterior shows little oxidation and the pittings are clean and sharp in outline. It is to be hoped that the Mexican Government, which with admirable liberality has already transferred to the School of Mines, Mexico, five of her largest meteorites, may also undertake the similar protection of this unique mass.

5. *The Origin of Eskers;* by W. O. CROSBY. Boston Soc. Nat. Hist., vol. 30, No. 3, pp. 375–411.—It is an accepted truth among glacialists that eskers are formed either by superglacial or subglacial streams, and the large majority of geologists believe they are of subglacial origin. Professor Crosby has reëxamined the whole subject and concludes that streams flowing upon the ice sheet rather than those flowing under it are responsible for most of the esker ridges.

6. *Ueber Hussakite (Xenotim) und einige andere seltene gesteinbildende Mineralien;* by H. RÖSLER. Zeitschr. f. Kryst., xxxvi, pp. 258–267.—Prismatic xenotime (hussakite) has been identified in the heavy residues of a large number (52) of European rocks and kaolins amongst the crystals usually referred to zircon, from which it was distinguished in part by the application of the magnesium test for phosphoric acid; in part by the hepar reaction for sulphuric acid with soda on charcoal, but for the most part by the difference in the strength of the double refraction in microscopic preparations. Owing to the elusive nature of all these tests when applied to microscopic crystals in microscopic quantities, it seems desirable to carefully verify these identifications before conclusions of such far-reaching consequences be definitely accepted.

Contrary to the observations of Derby, who only identified prismatic xenotime in a single case in scores of residues examined and who found the octahedral forms almost invariably accompanied by monazite, the author finds, in the rocks examined, the

prismatic forms of xenotime more abundant and widespread than the octahedral one and than monazite as well.

In addition to zircon, xenotime and monazite the author found anatase, regarded as secondary, in about half of the residues examined; dumortierite in two kaolins from 2-mica granite; chrysoberyl in seven kaolins (6 2-mica granites and 1 syenite) and one fresh 2-mica granite; staurolite in two kaolins from aplite, and andalusite in five kaolins from 2-mica granites.

III. Miscellaneous Scientific Intelligence.

1. *International Catalogue of Scientific Literature.* First Annual Issue. M. Botany, Part I, May, 1902. Pp. xiv, 378. D. Chemistry, Part I, June, 1902. Pp. xiv, 768.—These two volumes of the first annual issue of the International Catalogue of Scientific Literature, commencing with the year 1901, have recently appeared. This Catalogue is published for the International Council by the Royal Society of London, being an outgrowth of the well-known Catalogue of Scientific Papers relating to the scientific literature of the Nineteenth Century, published by the same Society. In the form which the plan has finally taken, each complete annual issue of the Catalogue will consist of seventeen volumes, one for each of the sections of science separately recognized. The set will be sold to the public for £18, individual volumes costing, according to size, from ten to thirty-five shillings. The director is Dr. H. Forster Morley, whose address is at the Central Bureau, 34 and 35 Southampton st., Strand, London, W.C. Twenty-nine Regional Bureaus have been arranged for, which are to furnish the material for the Catalogue; for the United States, communications are to be sent to Prof. S. P. Langley, Smithsonian Institution, Washington.

The method of classification and indeed all the details of the entire plan have been very carefully worked out, but only the outline can be given here. Each of the volumes issued consists of three parts: (*a*) Schedules and indexes in four languages, English, French, German and Italian; (*b*) an author's catalogue; (*c*) a subject catalogue. The subject catalogue is divided into sections, each of which is denoted by a four-figure number between 0000 and 9999. These numbers follow one another in order but all are not used, space being left for such additions to the system of classification as may be found necessary in future years. In the case of the two volumes now published, the material for 1901 being yet incomplete, the first part will be followed by a second part in a few months; in future, however, when the organization is complete, it is planned to issue a single annual volume only for each subject.

The breadth and completeness of this great scheme for putting within the reach of every worker in science a catalogue of all original contributions on the subject in which he is interested, in whatever form or place published, is worthy of the century with

which it commences and the Society under whose auspices it is published. It is to be hoped that the undertaking may not only receive all needed financial support, but also that editors and authors may inform themselves minutely as to the details of the plan, so that they may prepare subject-indexes for all papers at the time of their publication, thus diminishing very largely the subsequent labors of the collaborators.

2. *British Association.*—The annual meeting of the British Association for the Advancement of Science was held at Belfast during the week beginning September 10th. The meeting is described as having been very successful, about equal in numbers to that held in the same place in 1874, when the attendance was 1,951. The address of the President, Professor James Dewar, was of the highest interest (see Nature of Sept. 11), dealing, in addition to some general topics, with the subject of low temperature and the liquefaction of gases, to which he has personally contributed so much. We quote at length from the address in another place.

3. *Experiments in Aerodynamics;* by S. P. LANGLEY. Second edition, pp. 115 with ix plates. Washington, 1902. (Smithsonian Contributions to Knowledge, No. 801.)—This volume is essentially a reproduction of the first edition of this interesting memoir, which was issued in 1901 and noticed in this Journal in November of that year (vol. xlii, p. 427). Since its first publication, machines made on the principles here described have actually flown, which fact gives a practical interest to the subject; a description of the heavy steel flying machines is promised for some time in the future.

4. *Elementary Physical Geography;* by WILLIAM MORRIS DAVIS. Pp. x, 401, with numerous maps and illustrations (Ginn and Company.)—It is a pleasure to note the publication of a text-book which presents a subject in an interesting elementary form without the loss of scientific accuracy and a rational mode of treatment. Professor Davis's new text reduced from his "Physical Geography" is just such a book.

5. *The International Quarterly.*—The International Monthly, which since January, 1900 has had a highly successful career under the editorship of Mr. Frederick A. Richardson (Burlington, Vt.), will hereafter be continued as a quarterly with the same editorial direction. Each number will be more than double the size of the monthly, and will present articles of live interest by able writers at home and abroad. The September issue (pp. 1–214) of The International Quarterly begins vol. vi, of the series.

OBITUARY.

PROFESSOR RUDOLF VIRCHOW, the illustrious German anatomist, physiologist and anthropologist, the founder of cellular pathology, died at Berlin on September 5, in his eighty-first year.

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Kangasniemi, Finland. In this rock the concretions are light colored surrounded by bands of hornblende, the compactness of the concretion forming a strong contrast to the coarse crystalline structure of the matrix. The concretions range from 4 to 6 inches in diameter. Specimens from $6.00 to $30.00.

Quonochontaug, Rhode Island. This is the only Orbicular Granite we have ever seen from America. The concretions are mainly hornblende with granite centers intermediate in color between the above two, and average from 1 to 2½ inches in diameter; polished slices from $6.00 to $13.00.

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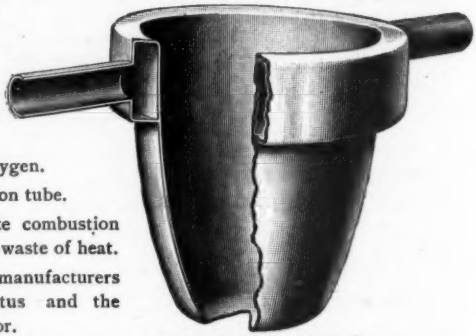

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J. WILEY & SONS, New York.—**System of Mineralogy** of J. D. DANA. 6th edit. by EDWARD S. DANA. lxiii, 1134 pp. large 8vo., 1892. $12.50. Appendix I, 75 pp, June 1899. $1.00. 5th edit., 1868, with three appendices, 1872, 1875, 1882. $5.00.—**Manual of Mineralogy & Lithology,** by J. D. DANA. 4th edition. 517 pp. 12mo., 1887, $2.00.—**Text-book of Mineralogy,** by E. S. DANA. Revised edition. 593 pp. 8vo., 1898, $4.00.—**Minerals and How to study them;** a book for beginners in Mineralogy, by E. S. DANA. 380 pp. 12mo., 1895, $1.50.—**Text-book of Elementary Mechanics,** by E. S. DANA. 300 pp. with numerous cuts, 12mo., 1881.

DODD & MEAD, New York.—**Corals and Coral Islands,** by J. D. DANA. 440 pp. 8vo. 3d ed., 1890.—**Characteristics of Volcanoes,** with contributions of facts and principles from the Hawaiian Islands, by J. D. DANA. 399 pp. 8vo. With illustrations, maps, etc. 1890.

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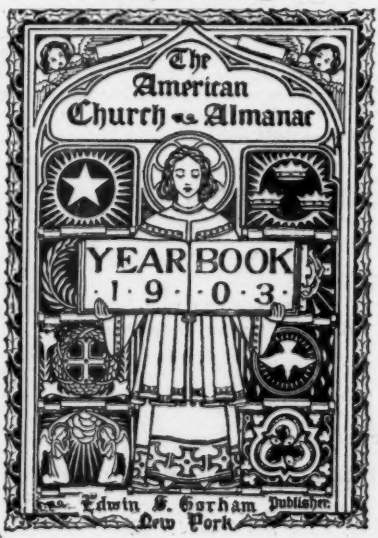

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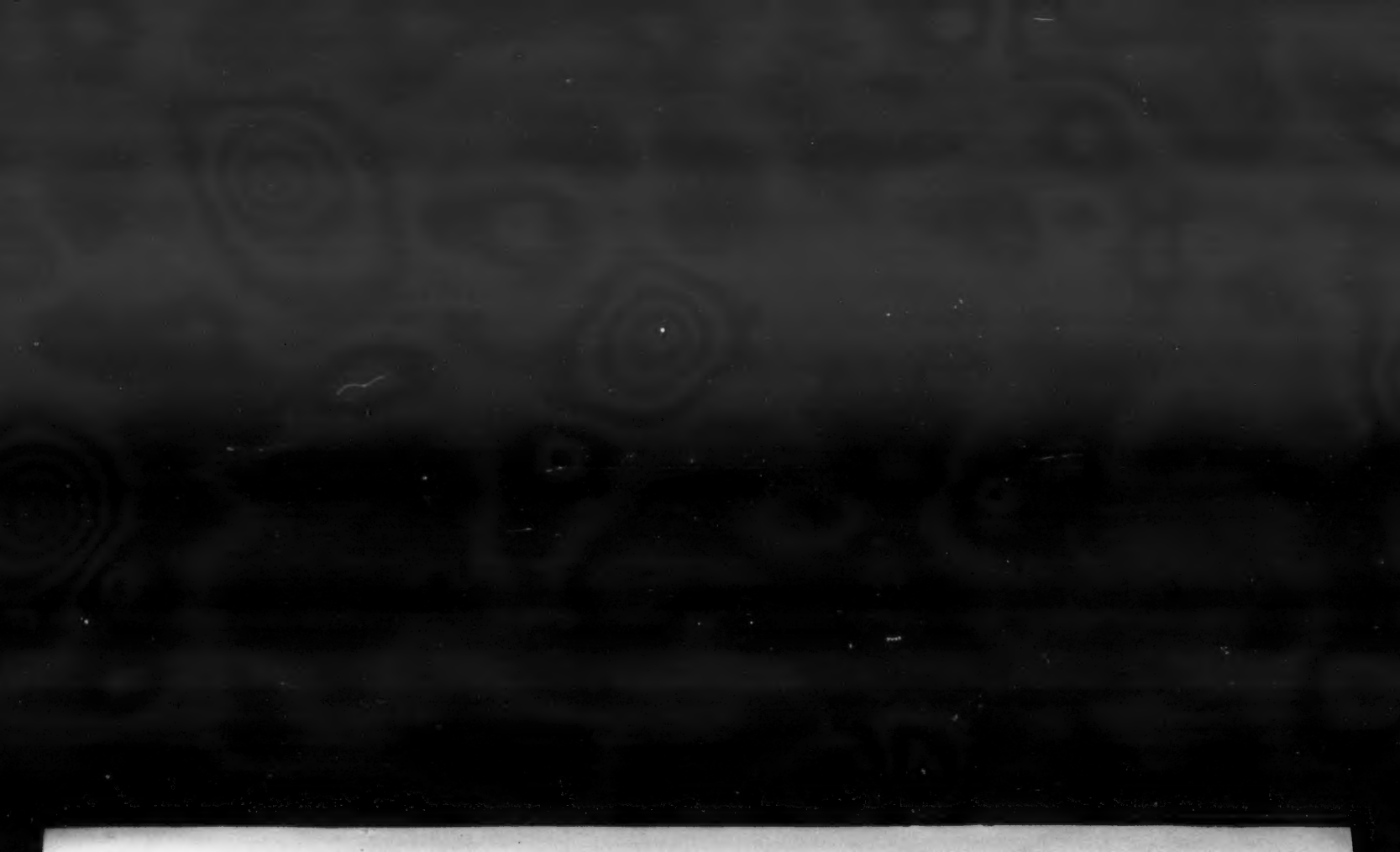
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